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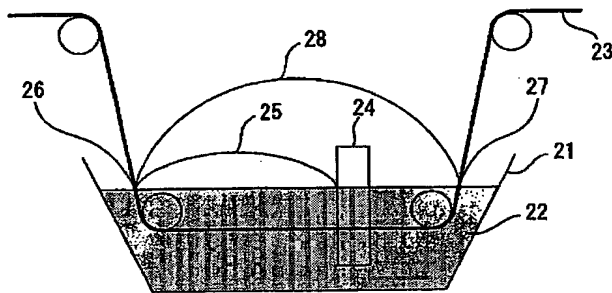
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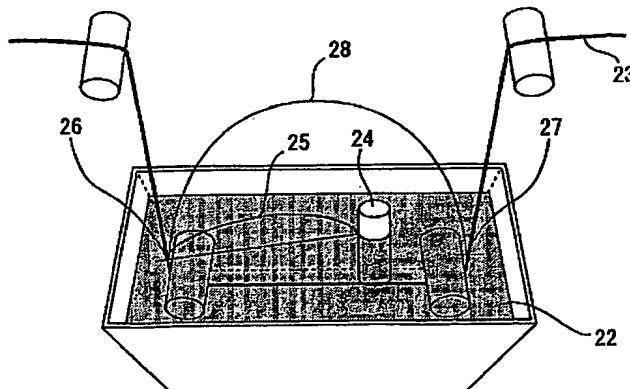
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[Continued on next page]

(54) Title: METHOD OF COATING A SQUARE WIRE AND AN INSULATED WIRE OF A SQUARE WIRE



(57) Abstract: It is an object of the present invention to provide a method of coating a square wire capable of providing an insulated wire of a square wire that has a high dielectric breakdown voltage. A method of coating a square wire comprising a step of carrying out cationic electrodeposition on a square wire to form an insulating film thereon, by using a cationic electrocoating that stored in an electrocoating bath, wherein the shifting speed of the square wire in the electrocoating bath is set in a range from 1 to 80 m/min; the shortest distance from a liquid-contact portion of the square wire onto the cationic electrocoating to an electrode is set longer than 1/2 of the total shift distance of the square wire from the liquid-contact portion of the square wire to a liquid-separation portion in the electrocoating bath, the cationic electrocoating contains a resin composition of which a hydratable functional group is reduced directly by electrons and passivated, resulting in deposition of a film, and the cationic electrocoating contains crosslinked resin particles.



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## DESCRIPTION

METHOD OF COATING A SQUARE WIRE AND AN INSULATED WIRE OF A SQUARE  
WIRE

5

## TECHNICAL FIELD

The present invention relates to a method of coating a square wire and an insulated wire of such a square wire.

10

## BACKGROUND ART

Insulated wires have been in wide use in the application areas such as electric and electronic equipment. These insulated wires generally have a structure in that an insulating film for protection and an enamel wire obtained by coating and  
15 baking an insulating coating containing organic resins such as various synthetic resins or natural resins is widely used.

As an insulating coating, insulating coatings formed by containing polyvinyl formal resin, polyurethane resin, polyester resin, polyester-imide resin, polyamide-imide resin  
20 or polyimide resin are generally used widely. In addition, preparation of an insulated wire is widely performed by electrodeposition using electrocoatings which have been previously used widely, and a round wire, which has a round shape in the cross-sectional profile, having an insulating film formed  
25 by using such the insulating coating or the electrocoating (see, for example, Japanese Kokai Publication Sho-48-49826 and Japanese Kokai Publication Hei-3-159014).

Here, in order to increase an occupancy ratio of an insulated wire or improve the function of an electric wire, square  
30 wires having a square shape in the cross-sectional profile have been developed, and insulated wires formed by using these square wires as articles to be coated have been developed. For example, when an insulated wire, formed by using a square wire, is used as a magnet wire or the like, it has the performances in that  
35 the size and the weight of the magnet can be reduced; a more

strong magnetic force can be attained; an electric current becomes large; and a heat releasing property is excellent. Therefore, these wires have drawn public attention in recent year.

5           However, in the case of an insulated wire obtained by applying the above-mentioned conventional insulating coating or electrocoating to a square wire, the film thickness of an insulating film formed on the edges becomes thin; consequently, an insulated wire having an adequate insulating property may  
10 not be attained.

          Moreover, when the electric wire of a square wire is applied, it becomes possible to improve the occupancy ratio because of its shape; however, when an insulating film is formed on the square wire by using a conventional insulating coating or  
15 electrocoating, the film thickness tends to become uneven between on edges and flat portions other than the edges, with the result that the film thickness of the insulating film formed on the edges becomes thin; consequently, the cross-sectional profile of the resulting insulated wire becomes different from the  
20 cross-sectional profile (square shape) of the article to be coated, resulting in a failure in improving the occupancy ratio.

          In the case when a square wire is used as an article to be coated, another problem that pinholes tend to occur particularly in the electrodeposition arises. When pinholes  
25 occur in the electrodeposited film, there is the possibility of deterioration in the insulating property.

          Therefore, there has been desired the development of a coating method which makes it possible to form an insulating film with a sufficient film thickness not only on flat portions,  
30 but also on edges, even when the article to be coated having edges such as a square wire is used, to prevent occurrence of pinholes, and consequently to provide an insulated wire having a high insulating property.

In view of the above-mentioned circumstances, it is an object of the present invention to provide a method of coating a square wire capable of providing an insulated wire of a square wire that has a high dielectric breakdown voltage.

5       The present invention relates to a method of coating a square wire comprising a step of:

          carrying out cationic electrodeposition on a square wire to form an insulating film thereon, by using a cationic electrocoating that stored in an electrocoating bath,

10       wherein the shifting speed of the square wire in the electrocoating bath is set in a range from 1 to 80 m/min;

          the shortest distance from a liquid-contact portion of the square wire onto the cationic electrocoating to an electrode is set longer than 1/2 of the total shift distance of the square  
15       wire from the liquid-contact portion of the square wire to a liquid-separation portion in the electrocoating bath,

          the cationic electrocoating contains a resin composition of which a hydratable functional group is reduced directly by electrons and passivated, resulting in deposition of a film,  
20       and

          the cationic electrocoating contains crosslinked resin particles.

          Preferably, the crosslinked resin particle is one of which a hydratable functional group is reduced directly by electrons  
25       and passivated.

          Preferably, the content of the crosslinked resin particles is 0.5 to 40 % by weight.

          Preferably, the crosslinked resin particle is obtained by emulsion polymerizing an  $\alpha,\beta$ -ethylenically unsaturated  
30       monomer mixture using a resin having an onium group as an emulsifier.

          Preferably, the resin having an onium group has 2 to 15 onium groups per one molecule.

          Preferably, the resin having an onium group is an acrylic  
35       resin or an epoxy resin.

Preferably, the onium group is an ammonium group or a sulfonium group.

Preferably, the acrylic resin or the epoxy resin, having the ammonium group or the sulfonium group, is obtained by adding  
5 a tertiary amine compound or sulfide and an organic acid to an acrylic resin or an epoxy resin, having an epoxy group, to convert the acrylic resin or the epoxy resin to a quaternary ammonium compound or a tertiary sulfonium compound.

Preferably, a number-average molecular weight of the  
10 acrylic resin or the epoxy resin, having an epoxy group, is 2000 to 20000.

Preferably, the resin composition has a sulfonium group and a propargyl group.

Preferably, the resin composition has a sulfonium group  
15 content of 5 to 400 milli moles, a propargyl group content of 10 to 495 milli moles and a total content of the sulfonium and propargyl groups of 500 milli moles or less, per 100 g of the solid matter in the resin composition.

Preferably, the resin composition includes an epoxy resin  
20 having a novolak cresol epoxy resin or a novolak phenol epoxy resin as a skeleton and having a number-average molecular weight of 700 to 5000, and

the resin composition also has a sulfonium group content of 5 to 250 milli moles, a propargyl group content of 20 to 395  
25 milli moles and a total content of the sulfonium and propargyl groups of 400 milli moles or less, per 100 g of the solid matter in the resin composition.

The present invention relates to an insulated wire of a square wire which is obtained by the above method of coating  
30 a square wire.

The present invention relates to a roll wire which is obtained from the insulated wire of a square wire.

The present invention also relates to a method of coating a square wire, comprising a step (I) of forming a first insulating  
35 film by cationic electrodeposition using a cationic

electrocoating, and a step (II) of forming a second insulating film on the first insulating film formed in the step (I) using an insulating coating,

5 wherein the shifting speed of the square wire in the electrocoating bath is set in a range from 1 to 80 m/min;

the shortest distance from a liquid-contact portion of the square wire onto the cationic electrocoating to an electrode is set longer than 1/2 of the total shift distance of the square wire from the liquid-contact portion of the square wire to a liquid-separation portion in the electrocoating bath, and

10 wherein said cationic electrocoating contains a resin composition of which a hydratable functional group is reduced directly by an electron and passivated, resulting in deposition of a film and

15 said cationic electrocoating and/or the insulating coating contains crosslinked resin particles.

Preferably, the cationic electrocoating contains crosslinked resin particles.

20 Preferably, the crosslinked resin particle is one of which a hydratable functional group is reduced directly by electrons and passivated.

Preferably, the content of the crosslinked resin particles is 0.5 to 40 % by weight in the coating.

25 Preferably, the crosslinked resin particle is obtained by emulsion polymerizing an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture using a resin having an onium group as an emulsifier.

Preferably, the resin having an onium group has 2 to 15 onium groups per one molecule.

30 Preferably, the emulsifier is an acrylic resin or an epoxy resin.

Preferably, the onium group is an ammonium group or a sulfonium group.

35 Preferably, the acrylic resin or the epoxy resin, having the ammonium group or the sulfonium group, is obtained by adding

a tertiary amine compound or sulfide and an organic acid to an acrylic resin or an epoxy resin, having an epoxy group, to convert the acrylic resin or the epoxy resin to a quaternary ammonium compound or a tertiary sulfonium compound.

5            Preferably, a number-average molecular weight of the acrylic resin or the epoxy resin, having an epoxy group, is 2000 to 20000.

Preferably, the resin composition has a sulfonium group and a propargyl group.

10 Preferably, the resin composition has a sulfonium group content of 5 to 400 milli moles, a propargyl group content of 10 to 495 milli moles and a total content of the sulfonium and propargyl groups of 500 milli moles or less, per 100 g of the solid matter in the resin composition.

15 Preferably, the resin composition includes an epoxy resin having a novolak cresol epoxy resin or a novolak phenol epoxy resin as a skeleton and having a number-average molecular weight of 700 to 5000, and  
the resin composition also has a sulfonium group content of 5  
20 to 250 milli moles, a propargyl group content of 20 to 395 milli moles and a total content of the sulfonium and propargyl groups of 400 milli moles or less, per 100 g of the solid matter in the resin composition.

The present invention relates to an insulated wire of a  
25 square wire which is obtained by the above method of coating  
a square wire.

The present invention relates to a roll wire which is obtained from the insulated wire of a square wire.

30 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows an example of a schematic view of a cross section of an insulated wire of a square wire obtained by the method of coating a square wire in accordance with the present invention.

35 Fig. 2 shows an example of a schematic view of a cross



section of an insulated wire of a square wire obtained in the case of using no crosslinked resin particle.

Fig. 3 shows an example of a schematic view of an electrocoating bath to be used in the method of coating a square wire of the present invention.

Fig. 4 shows an example of a schematic view of an electrocoating bath to be used in the method of coating a square wire of the present invention.

Fig. 5 shows an example of a schematic view of a cross section of an insulated wire of a square wire obtained by the second method of coating a square wire in accordance with the present invention.

Fig. 6 shows an example of a schematic view of a cross section of an insulated wire of a square wire obtained in the case of using no crosslinked resin particle.

#### EXPLANATION OF THE NUMERICAL SYMBOLS

- |    |   |
|----|---|
| 1  | square wire   |
| 2  | insulating film   |
| 20 | 3 insulated wire  |
|    | 4 edges   |
|    | 5 insulated wire of a square wire                             |
|    | 6 flat portion  |
|    | 7 square wire   |
| 25 | 8 first insulating film                                       |
|    | 9 second insulating film                                      |
|    | 10 insulated wire of a square wire                            |
|    | 11 edges  |
|    | 12 insulated wire of a square wire                            |
| 30 | 13 flat portion   |
|    | 21 electrocoating bath  |
|    | 22 electrocoating   |
|    | 23 square wire  |
|    | 24 electrode  |
| 35 | 25 shortest distance from liquid-contact portion to electrode |

- in electrocoating bath
- 26 liquid-contact portion
- 27 liquid-separation portion
- 28 shift distance from liquid-contact portion to
- 5 liquid-separation portion in electrocoating bath

#### DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the present invention will be described in detail.

- 10 Since the method of coating a square wire of the present invention uses a wire having a square shape in the cross-sectional profile, it becomes possible to greatly improve the occupancy ratio because of its shape in comparison with an insulated wire that uses a round wire as its article to be coated. In the case
- 15 when an insulating film is formed on the square wire by using a conventional insulating coating, the film thickness tends to become uneven between on edges and flat portions other than the edges, with the result that the film thickness of the insulating film formed on the edge becomes thin; consequently, the
- 20 cross-sectional profile of the resulting insulated wire becomes different from the shape of the square wire, making it difficult to sufficiently improve the occupancy ratio in the case of simply using the square wire. On the other hand, in the method of coating a square wire of the present invention, a cationic electrocoating
- 25 containing crosslinked resin particles is used so as to perform cationic electrodeposition; therefore, it becomes possible to form an insulating film with a sufficient film thickness not only on the flat portions, but also on the edges. Thus, the application of the method of coating a square wire of the present
- 30 invention makes the cross-sectional profile less susceptible to variations upon forming an insulated wire of a square wire, and consequently improves the occupancy ratio of the resulting insulating wire of a square wire. For this reason, when the resulting insulated wire formed by a square wire is used as a
- 35 magnet wire or the like, the size and the weight of the magnet

can be reduced and a more strong magnetic force can be attained in comparison with the case in which a round wire having the same volume is used as the article to be coated. Moreover, it becomes possible to provide large electric current and enhance a heat releasing property; thus, such the insulated wire is more desirably used.

The crosslinked resin particle has the function of providing a thixotropic property in the cationic electrocoating. Thus, in baking and curing the applied film to form an insulating film, an insulating film can be formed in a sufficient film thickness not only at flat portions even at edges of a square wire and, as a result, an insulated wire having a high dielectric breakdown voltage can be attained.

For example, when an article to be coated is electrodeposited using the cationic electrocoating containing the crosslinked resin particles, the function of the crosslinked resin particle to provide a thixotropic property allows the whole surface of the article to be coated, that is, the whole surface including the edges to be coated with a sufficient insulating film and an insulated wire of a square wire to be obtained to be provided with a high dielectric breakdown voltage.

When the cationic electrocoating does not contain the crosslinked resin particles or contains non-crosslinked resin particles instead of the crosslinked resin particles, an insulated wire of a square wire having a high dielectric breakdown voltage may not be obtained since edges cannot be coated in a sufficient film thickness.

Fig. 1 shows an example of a conceptual view of a cross section of the insulated wire of a square wire obtained by electrodeposition using the cationic electrocoating containing the crosslinked resin particles in the method of coating a square wire in accordance with the present invention. Fig. 1 shows an insulated wire of a square wire 3 which is obtained by forming an insulating film 2, to be formed by electrodeposition using the cationic electrocoating, on a square wire 1. The insulated

wire of a square wire 3, obtained in the case where the cationic electrocoating containing the crosslinked resin particles is used, is provided with the insulating film 2 with a sufficient film thickness on flat portions and edges 4 of the square wire 1. Accordingly, the insulated wire of a square wire 3 obtained by the above coating method has a high dielectric breakdown voltage.

On the other hand, Fig. 2 shows an example of a conceptual view of a cross section of the insulated wire obtained by forming an insulating film using a cationic electrocoating containing no crosslinked resin particles. The insulated wire of a square 5, obtained in the case where a cationic electrocoating containing no crosslinked resin particles is used, is not provided with the insulating film 2 with a sufficient film thickness on the edges 4 of the square wire 1. Consequently, the insulated wire of a square wire 5 obtained by the above coating method has a lower dielectric breakdown voltage in comparison to the insulated wire obtained by the method of coating a square wire in accordance with the present invention.

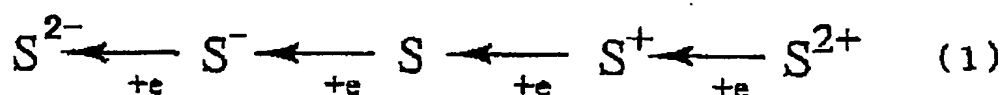
The crosslinked resin particle is not particularly limited, but includes a compound obtained by a so-called emulsion method in which a polymerizable monomer is crosslinked in an aqueous medium while being emulsion polymerized in the presence of a resin having a emulsifying power and an initiator, and a compound obtained by a so-called NAD method in which a polymerizable monomer is crosslinked while being copolymerized in a mixed solution of an organic solvent and a dispersion-stable resin soluble in an organic solvent, which are methods well known to those skilled in the art.

As a volume-average particle diameter of the crosslinked resin particles, it is preferred that specifically, a lower limit is  $0.05\ \mu\text{m}$  and an upper limit is  $1\ \mu\text{m}$ . When it is less than  $0.05\ \mu\text{m}$ , the thickness of film at the edges may become insufficient, and when it exceeds  $1\ \mu\text{m}$ , an appearance of the insulating film may be deteriorated. More preferably, the lower limit is  $0.07$

μm and the upper limit is 0.5 μm. This volume-average particle diameter can be controlled by adjusting, for example, the composition or the polymerization conditions of a polymerizable monomer. The volume-average particle diameter can be  
 5 determined, for example, by a laser-light-scattering method and the like.

The crosslinked resin particle is preferably one of which a hydratable functional group is reduced directly by electrons and passivated. It is possible to provide a good thixotropic  
 10 property for a coating by using such crosslinked resin particles. Thereby, an insulating film can be sufficiently formed even at edges of a square wire, and an insulated wire having a high dielectric breakdown voltage can be attained.

In the present invention, the mechanism of deposition of  
 15 the crosslinked resin particle on the cathode as caused by voltage application is represented by the following formula (1). The crosslinked resin particle is passivated to be deposited by providing the hydratable functional group in the crosslinked resin particle (substrate; expressed by "S" in the formula) with  
 20 electrons on the cathode.



That is, when the reaction represented by the above formula (1) occurs, the hydratable functional group existing in the  
 25 crosslinked resin particle in the cationic electrocoating is directly reduced on the cathode, resulting in insolubilization and deposition of the crosslinked resin particle. The film deposited according to this mechanism has a high dielectric breakdown voltage.

30 In particular, the crosslinked resin particle is preferably obtained by emulsion polymerizing an α,β-ethylenically unsaturated monomer mixture using a resin

having an onium group as an emulsifier. By containing such a crosslinked resin particle, it is possible to coat flat portions and edges sufficiently with an insulating film and to obtain an insulated wire having a higher dielectric breakdown voltage.

5            Preferably, the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture generally contains poly(meth)acrylate having two or more  $\alpha,\beta$ -ethylenically unsaturated bonds in a molecule in order to crosslink the resin particle. The content of the poly(meth)acrylate having two or  
10 more  $\alpha,\beta$ -ethylenically unsaturated bonds in a molecule is preferably 5 % by weight (lower limit) to 15 % by weight (upper limit) relative to 100 % by weight of total solid matter in the  $\alpha,\beta$ -ethylenically unsaturated monomer mixture. When this content is less than 5 % by weight, crosslinking of the resin  
15 particle does not adequately proceed, and when it exceeds 15 % by weight, crosslinking of the resin particle proceeds excessively; therefore, physical properties of an insulating film to be obtained may be deteriorated.

As the above-mentioned poly(meth)acrylate having two or  
20 more  $\alpha,\beta$ -ethylenically unsaturated bonds in a molecule, there may be given, for example, a compound having a structure in which a plurality of (meth)acrylic acids combine with dihydric or higher alcohol in the form of an ester linkage, and the like. Examples of the above-mentioned compound having a structure in  
25 which a plurality of (meth)acrylic acids combine with dihydric or higher alcohol in the form of an ester linkage may include ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylol propane  
30 tri(meth)acrylate, and the like. These compounds may be used alone or in combination of two or more kinds of them.

The  $\alpha,\beta$ -ethylenically unsaturated monomer mixture contains a general  $\alpha,\beta$ -ethylenically unsaturated monomer besides the above-mentioned poly(meth)acrylate. As the  
35 above-mentioned general  $\alpha,\beta$ -ethylenically unsaturated monomer,

there may be given a compound having a reactive functional group and a compound having no reactive functional group.

Examples of the  $\alpha,\beta$ -ethylenically unsaturated monomer having the reactive functional group may include hydroxyethyl  
5 (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, allyl alcohol, methacrylic alcohol, hydroxyl group-containing compounds such as  $\epsilon$ -caprolactam adduct of hydroxyethyl (meth)acrylate; epoxy group-containing compounds such as glycidyl (meth)acrylate, and the like.

10 When the  $\alpha,\beta$ -ethylenically unsaturated monomer having the reactive functional group is contained in the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture, the content of the  $\alpha,\beta$ -ethylenically unsaturated monomer having the reactive functional group is preferably 20 % by weight or less relative  
15 to 100 % by weight of the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture. When the content exceeds 20 % by weight, the water resistance of a film to be obtained may be deteriorated. Both of the hydroxyl group value or epoxy value of the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture in this case is preferably 20 or less. When it exceeds  
20 20, the water resistance or the insulating property of a film to be obtained may be deteriorated.

On the other hand, examples of the  $\alpha,\beta$ -ethylenically unsaturated monomer having no reactive functional group may  
25 include (meth)acrylic ester such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isobornyl  
30 (meth)acrylate, cyclohexyl (meth)acrylate, t-butylcyclohexyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, and dihydrodicyclopentadienyl (meth)acrylate; polymerizable amide compounds such as (meth)acrylamide, N-methylol (meth)acrylamide, N-butoxymethyl (meth)acrylamide,  
35 N,N-dimethyl (meth)acrylamide, N,N-dibutyl (meth)acrylamide,

N,N-dioctyl(meth)acrylamide, N-monobutyl(meth)acrylamide, N-monooctyl(meth)acrylamide, 2,4-dihydroxy-4'-vinylbenzophenone, N-(2-hydroxyethyl)acrylamide, and  
5 N-(2-hydroxyethyl)methacrylamide; polymerizable aromatic compounds such as styrene,  $\alpha$ -methylstyrene, vinyl ketone, t-butylstyrene, p-chlorostyrene, and vinyl naphthalene; polymerizable nitriles such as acrylonitrile, and methacrylonitrile; ethylene, propylene and the like; vinyl  
10 esters (e.g.,  $\alpha$ -olefins such as vinyl acetate and vinyl propionate); diens such as butadiene and isoprene.

In the resin having an onium group used as an emulsifier in emulsion polymerization for preparing the crosslinked resin particle, the number of onium groups is preferably 2 to 15 per  
15 one molecule. When the number of onium groups is less than 2 per one molecule, the stability of dispersion may be deteriorated, and when it exceeds 15, the water resistance of an insulating film to be obtained may be deteriorated. In addition, as the onium group, there may be given an ammonium group or a sulfonium  
20 group, but the ammonium group is preferable from the viewpoint of water resistance.

Examples of the resin having the ammonium group or sulfonium group may include an acrylic resin, a polyester resin, an epoxy resin, a urethane resin and the like. An acrylic resin  
25 or an epoxy resin is preferable from the viewpoint of design. The above-mentioned acrylic resin or epoxy resin can be attained by various methods but it can be easily obtained by adding a tertiary amine compound or sulfide and an organic acid to an acrylic resin or an epoxy resin, having an epoxy group, to convert  
30 the acrylic resin or the epoxy resin to a quaternary ammonium compound or a tertiary sulfonium compound. In addition, this conversion to a quaternary ammonium compound or a tertiary sulfonium compound may be carried out by previously preparing a mixture of a tertiary amine compound and an organic acid or  
35 sulfide and an organic acid and adding this mixture to the acrylic



resin or the epoxy resin, having an epoxy group, as an ammonium quaternizing agent or a sulfonium tertiarizing agent.

An acrylic resin having an epoxy group, which is used for conversion to a quaternary ammonium compound or a tertiary sulfonium compound, can be obtained by polymerizing a mixed monomer solution comprising an  $\alpha,\beta$ -ethylenically unsaturated monomer having an epoxy group such as glycidyl (meth)acrylate and another  $\alpha,\beta$ -ethylenically unsaturated monomer according to an ordinary technique. In this method of conversion to a quaternary ammonium compound or a tertiary sulfonium compound, the amount of the  $\alpha,\beta$ -ethylenically unsaturated monomer having an epoxy group may be determined depending on the number of onium groups described above because an epoxy group is converted to an onium group by being ring-opened with a tertiary amine compound or sulfide. The above-mentioned another  $\alpha,\beta$ -ethylenically unsaturated monomer refers to the above-mentioned general  $\alpha,\beta$ -ethylenically unsaturated monomer, for example, in the  $\alpha,\beta$ -ethylenically unsaturated monomer mixture described above.

As the above-mentioned epoxy resin, there are suitably used those having at least two epoxy groups in one molecule, including, for example, polyepoxy resins such as epi-bis-epoxy resins; modifications thereof obtained by extending its chain with diol, dicarboxylic acid or diamine; epoxidized polybutadiene; novolak phenol polyepoxy resins; novolak cresol polyepoxy resins; polyglycidyl acrylate; polyglycidyl ethers of aliphatic polyols or polyethers polyol; and polyglycidyl esters of polybasic carboxylic acids. In particular, novolak phenol polyepoxy resins, novolak cresol polyepoxy resins and polyglycidyl acrylate are preferable because of the ease of polyfunctionalization for enhancing curability. In addition, part of the above-mentioned epoxy resin may be a monoepoxy resin.

A number-average molecular weight of the above-mentioned acrylic resin or epoxy resin, having an epoxy group, is preferably 2000 to 20000. When the number-average molecular weight is less than 2000, the film thickness of film at the edges may be

insufficient, and when it exceeds 20000, a rise in viscosity of an emulsifier may become a problem.

The tertiary amine compound for introducing above-mentioned ammonium group in an acrylic resin or an epoxy resin is not particularly limited, but includes trimethylamine, triethylamine, tributylamine, trioctylamine, dimethylethanolamine, methyldiethanolamine, and the like. Incidentally, the amount of the tertiary amine compound may be determined in conformity with the amount of ammonium group to be introduced.

The sulfide for introducing above-mentioned sulfonium group in an acrylic resin or an epoxy resin is not particularly limited, and examples thereof may include aliphatic sulfides, aliphatic-aromatic mixed sulfides, aralkyl sulfides, and cyclic sulfides. Specific examples thereof may include diethyl sulfide, dipropyl sulfide, dibutyl sulfide, dihexyl sulfide, diphenyl sulfide, ethyl phenyl sulfide, tetramethylene sulfide, pentamethylene sulfide, thiodiethanol, thiodipropanol, thiodibutanol, 1-(2-hydroxyethylthio)-2-propanol, 1-(2-hydroxyethylthio)-2-butanol, and 1-(2-hydroxyethylthio)-3-butoxy-1-propanol.

An organic acid used for conversion to a quaternary ammonium compound or a tertiary sulfonium compound is not particularly limited, and examples thereof may include formic acid, acetic acid, lactic acid, propionic acid, boric acid, butyric acid, dimethylolpropionic acid, hydrochloric acid, sulfuric acid, phosphoric acid, N-acetylglycine, and N-acetyl- $\beta$ -alanine. In particular, lactic acid, acetic acid and dimethylolpropionic acid are preferable in point of the stability in emulsifying.

In this conversion to a quaternary ammonium compound or a tertiary sulfonium compound, the molar ratio among an epoxy group, a tertiary amine compound or sulfide, and an organic acid in an acrylic resin or an epoxy resin having an epoxy group is preferably 1 : 1 : 1 to 1 : 1 : 2. A reaction of conversion

to a quaternary ammonium compound or a tertiary sulfonium compound is generally conducted over 2 to 10 hours and may be heated to 60 to 100°C as required.

The crosslinked resin particle, contained in a cationic electrocoating composition, in the present invention can be obtained by conducting emulsion polymerization using a resin having an onium group obtained in such a manner as described above as an emulsifier. The emulsion polymerization can be conducted using a method being usually well known. For example, this can be conducted by dissolving an emulsifier in an aqueous medium including water, or an organic solvent such as alcohol or the like as required and adding the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture and an initiator dropwise to this solution under being heated and stirred.

An  $\alpha,\beta$ -ethylenically unsaturated monomer mixture previously emulsified with an emulsifier and water may be added dropwise similarly.

The above-mentioned emulsion polymerization is preferably conducted following a procedure in which an emulsifier is dissolved in an aqueous medium and after an initiator is added dropwise to this solution under being heated and stirred, part of the  $\alpha,\beta$ -ethylenically unsaturated monomer is added dropwise and, then, the rest of  $\alpha,\beta$ -ethylenically unsaturated monomer mixture, which has been previously emulsified with an emulsifier and water, is added dropwise. By emulsion polymerizing using this procedure, the deviation from a desired particle diameter is reduced and preferable crosslinked resin particles can be obtained.

The initiator is not particularly limited, and preferable examples thereof may include oily azo compounds (e.g., azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2-(2-imidazoline-2-yl)propane), 2,2'-azobis(2,4-dimethylvaleronitrile) and the like); aqueous compounds (e.g., 4,4'-azobis(4-cyanovalerate), 2,2'-azobis(N-(2-carboxyethyl)-2-methylpropionamidine) of

anionic compounds, and 2,2'-azobis(2-methylpropionamidine) of cationic compounds; oily redox peroxides (e.g., benzoyl peroxide, p-chlorobenzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate, and the like); and aqueous peroxides (e.g.,  
5 potassium persulfate, ammonium persulfate, and the like).

The resin having an onium group, described above, is used as the emulsifier. Further, it is possible to use compounds usually used by those skilled in the art or reactive emulsifiers, e.g., ANTOXMS-60 (made by Nippon Surfactant Co., Ltd.), ELEMNOL  
10 JS-2 (made by Sanyo Kasei Co., Ltd.), ADEKARIA SOAP NE-20 (made by Asahi Denka Co., Ltd.), and AQUARON HS-10 (made by Daiichi Kogyo Seiyaku Co., Ltd.), in combination with the resin having an onium group. Here, the above-mentioned reactive emulsifier is assumed to be not included in an  $\alpha,\beta$ -ethylenically unsaturated  
15 monomer contained in the monomer mixture described above.

The ratio by weight between the above-mentioned resin having an onium group and the above-mentioned  $\alpha,\beta$ -ethylenically unsaturated monomer mixture (weight of the resin having an onium group/weight of the  $\alpha,\beta$ -ethylenically unsaturated monomer  
20 mixture) is preferably 5:95 to 50:50. When the above-mentioned ratio by weight is out of the above range, the appearance of an insulating film may be deteriorated.

In the above emulsion polymerization, mercaptan such as lauryl mercaptan and a chain transfer agent such as  
25  $\alpha$ -methylstyrene dimer may be used as required in order to adjust a molecular weight.

A reaction temperature in the above emulsion polymerization depends on an initiator, and for example, it is preferably 60 to 90°C in azo initiators and 30 to 70°C in redox  
30 initiators. Generally, a reaction time is 1 to 8 hours. The ratio of the initiator to the total amount of the  $\alpha,\beta$ -ethylenically unsaturated monomer mixture is generally 0.1 % by weight (lower limit) to 5 % by weight (upper limit). Preferably, the above lower limit is 0.2 % by weight and the  
35 above upper limit is 2 % by weight.

The cationic electrocoating in the present invention preferably contains the crosslinked resin particle obtained in a manner described above in an amount of 0.5 to 40 % by weight relative to the resin solid matter in the coating composition.

5 When the above-mentioned content of the crosslinked resin particle is less than 0.5 % by weight, the thickness of film at the edges may become insufficient, and when it exceeds 40 % by weight, an appearance of the insulating film may be deteriorated. The above content is more preferably 1 to 30 %  
10 by weight. Here, when the crosslinked resin is obtained by the NAD method, the content of the crosslinked resin particle includes the polymerizable monomer crosslinked through copolymerization and the dispersion-stable resin.

The method of coating a square wire in accordance with  
15 the present invention comprises the step of forming an insulating film by cationic electrodeposition using a cationic electrocoating.

Since the cationic electrocoating used in the present invention contains the above-mentioned crosslinked resin  
20 particles, an insulated wire having a higher dielectric breakdown voltage than an insulated wire prepared from a conventional cationic electrocoating can be attained.

In the method of coating a square wire of the present invention, upon coating, a ratio among factors, such as the  
25 shifting speed of the square wire to be coated, the shortest distance from the liquid-contact portion to the electrode in the electrocoating bath and the shift distance from the liquid-contact portion to the liquid-separation portion in the electrocoating bath, is set in a specific range; thus, it becomes  
30 possible to prevent occurrence of pinholes in the electrodeposited film.

The electrodeposition apparatus that can be used may be a horizontal-electrodeposition apparatus in which  
electrodeposition is carried out while an electric wire being  
35 an article to be coated is pulled horizontally, or a vertical

electrodeposition apparatus in which an electric wire being an article to be coated are introduced into the electrocoating bath from the bottom thereof and pulled out from the top of the electrocoating bath.

5 Normally, the electrodeposition for an electric wire are carried out continuously by using electrodeposition coating apparatus shown in Figs. 3 and 4. For example, the electrodeposition apparatus, shown in Fig. 3, is provided with a horizontal-electrodeposition bath in which electrodeposition  
10 is carried out while an electric wire is pulled horizontally. In the bath, an electrode is placed, and by applying a voltage across a square wire to be coated and the electrode, the electrodeposition is carried out.

For example, the electrodeposition apparatus, shown in  
15 Fig. 4, is provided with a vertical electrodeposition bath in which an electrodeposition is carried out while shifting the electric wire vertically. Both of the coating processes using the vertical electrodeposition bath and the horizontal-electrodeposition bath are carried out based upon  
20 the same mechanism.

In the above-mentioned electrodeposition apparatus, the square wire 23 to be coated is continuously subjected to coating processes while being always shifted; and the shifting speed of the square wire 23 is set in a range from 1 to 80 m/min during  
25 the coating processes. The shifting speed of less than 1 m/min causes a reduction in the treating speed, and the subsequent reduction in the productivity. The shifting speed exceeding 80 m/min tends to cause pinholes and the subsequent degradation in the insulating property. The above-mentioned shifting speed  
30 is preferably set in a range from 5 to 40 m/min.

Moreover, the ratio between the shortest distance from the liquid-contact portion 26 to the electrode 24 in the electrodeposition bath 21 and the shift distance from the liquid-contact portion 26 to the solution-separation portion  
35 27 is set to greater than 1/2. Here, the shortest distance from

the liquid-contact portion 26 to the electrode 24 in the electrodeposition bath 21 refers to the shortest distance from the portion at which, upon electrodeposition, the square wire 23 is made in contact with the interface of the electrocoating 22 when proceeding into the electrodeposition bath 21 to the electrode 24. This distance is indicated by reference numeral 25 in Figs. 3 and 4 respectively.

The shift distance from the liquid-contact portion 26 to the solution-separation portion 27 in the electrodeposition bath 21 refers to a distance from the portion at which, upon electrodeposition, the square wire 23 is made in contact with the interface of the electrocoating 22 when proceeding into the electrodeposition bath 21 to the portion at which it is made in contact with the interface of the electrocoating 22 when getting out of the electrodeposition bath 21. Here, since this distance is a shift distance of the square wire 23, it is not a straight distance from the liquid-contact portion 26 to the solution-separation portion 27, but a shift distance including diagonal shifts and curved shifts. This distance is indicated by reference numeral 28 in Figs. 3 and 4 respectively.

The absolute values of these values may be set in accordance with various factors such as the size of the electrodeposition bath 21 to be used, the composition of the coating to be used and the line speed; however, the ratio between the shortest distance from the liquid-contact portion 26 to the electrode 24 in the electrodeposition bath 21 and the shift distance from the liquid-contact portion 26 to the solution-separation portion 27 in the electrodeposition bath 21 needs to be set to greater than 1/2. When the electrode 24 is too close to the liquid-contact portion 26, pinholes tend to occur. The ratio between the shortest distance from the liquid-contact portion 26 to the electrode 24 in the electrodeposition bath 21 and the shift distance from the liquid-contact portion 26 to the solution-separation portion 27 in the electrodeposition bath 21 is more preferably set to greater than 2/3.

The cationic electrocoating used in the present invention contains a resin composition of which a hydratable functional group is reduced directly by electrons and passivated, resulting in deposition of a film. The mechanism of deposition on the cathode as caused by voltage application is represented by the  
5 above-mentioned formula (1); thereby, a film is deposited.

In the method of coating a square wire of the present invention, preferably, the resin composition has a sulfonium group and a propargyl group. By using the resin composition  
10 having a sulfonium group and a propargyl group, an insulated wire of a square wire having a higher dielectric breakdown voltage can be attained.

The resins composing the above resin composition may contain both a sulfonium group and a propargyl group in each molecule, but it does not necessarily do so. Thus, for example,  
15 the resins may have only either the sulfonium group or the propargyl group in each molecule. In the latter case, however, the whole resin composition has both of these two kinds of curable functional groups. That is, the above resin composition may  
20 comprise any resin containing sulfonium group and propargyl group, a mixture of a resin having only a sulfonium group(s) and a resin having only a propargyl group(s), or a mixture of all of these kinds of resins. It is herein defined in the above sense that the resin composition has both sulfonium and propargyl groups.

25 The sulfonium group is a hydratable functional group in the resin composition. When an electric voltage or current exceeding a certain level is applied to the sulfonium group in the electrodeposition step, the group is subjected to an electrolytic reduction on the electrode; thereby, the ionic group  
30 disappears and the sulfonium group can be irreversibly passivated.

It is considered that, in this electrodeposition step, the electrode reaction provoked generates the hydroxide ion, and the sulfonium group holds the hydroxide ion, with the result  
35 that an electrolytically generated base is formed in the



electrodeposited film. This electrolytically generated base can convert the propargyl group existing in the electrodeposited film and being low in reactivity upon heating to the allene bond high in reactivity upon heating.

5           A resin forming the skeleton of the resin composition is not particularly limited, but an epoxy resin is favorably used. As the above-mentioned epoxy resin, there may, for example, the epoxy resin described previously.

10           Preferably, the resin composition includes a resin having the epoxy resin as a skeleton and has a number-average molecular weight of 500 (lower limit) to 20000 (upper limit). When it is less than 500, the coating efficiency in the electrodeposition step will be poor, and when it exceeds 20000, a good film cannot be formed on the surface of a substrate. As for the  
15           number-average molecular weight, a more preferable molecular weight can be selected in accordance with the resin skeleton. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the lower limit is preferably 700 and the upper limit is preferably 5000.

20           Preferably, the sulfonium group content in the resin composition is within a range of 5 milli moles (lower limit) to 400 milli moles (upper limit) per 100 g of the solid matter in the resin composition provided that the total content of the sulfonium and propargyl groups conditions to be mentioned later  
25           herein are satisfied. When this content is less than 5 milli moles per 100 g of the solid matter, curability cannot be adequately exerted, and hydratability and bath stability are deteriorated. When it exceeds 400 milli moles per 100 g of the solid matter, the film deposition on the surface of a substrate  
30           becomes poor. As for the sulfonium group content, a more preferable content can be selected in accordance with the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the above lower limit is preferably 5 milli moles, more preferably 10 milli moles  
35           per 100 g of the solid matter in the resin composition. In

addition, the above upper limit is preferably 250 milli moles, more preferably 150 milli moles per 100 g of the solid matter in the resin composition.

5 The propargyl group of the resin composition acts as a curable functional group in the cationic electrocoating.

Preferably, the propargyl group content in the resin composition is within a range of 10 milli moles (lower limit) to 495 milli moles (upper limit) per 100 g of the solid matter in the resin composition provided that the total content of the  
10 sulfonium and propargyl groups conditions to be mentioned later herein are satisfied. When this content is less than 10 milli moles per 100 g of the solid matter, curability cannot be sufficiently exerted, and when it exceeds 495 milli moles per 100 g of the solid matter, the hydration stability in the case  
15 of being used as an electrocoating may be affected. As for the propargyl group content, a more preferable content can be selected in accordance with the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the above lower limit is more preferably  
20 20 milli moles and the above upper limit is more preferably 395 millimoles, per 100 g of the solid matter in the resin composition.

The total content of the sulfonium and propargyl groups, in the above resin composition, is preferably 500 milli moles or less per 100 g of the solid matter in the resin composition.  
25 When this content exceeds 500 milli moles per 100 g of the solid matter, a resin may not be attained in fact or a desired performance may not be attained. As for the total content of the sulfonium and propargyl groups, in the above resin composition, a more preferable content can be selected in accordance with the resin  
30 skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the total content is more preferably 400 milli moles or less per 100 g of the solid matter in the resin composition.

Part of the propargyl group in the resin composition may  
35 be converted to an acetylide. An acetylide is a salt-like

acetylated metal compound. As for the content of the propargyl group to be converted to an acetylide in the resin composition, preferably, the lower limit is 0.1 milli mole and the upper limit is 40 milli moles, per 100 g of the solid matter in the resin composition. When this content is less than 0.1 milli mole per 100 g of the solid matter, the effect of the conversion to an acetylide are not sufficiently exerted, and when it exceeds 40 milli moles, per 100 g of the solid matter, the conversion to an acetylide is difficult. As for this content, a more preferable range can be selected in accordance with the metal species employed.

A metal contained in the propargyl group converted to an acetylide is not particularly limited as long as it presents a catalytic action, and example thereof may include transition metals such as copper, silver and barium. If considering the conformity with an environment, copper and silver are preferable, and copper is more preferable from the viewpoint of the availability. When copper is used as the above-mentioned metal, the content of the propargyl group to be converted to an acetylide in the above resin composition is more preferably 0.1 to 20 milli moles per 100 g of the solid matter in the resin composition.

By converting part of the propargyl group in the above resin composition to an acetylide, a curing catalyst can be introduced into the resin. When the resin composition is prepared in this manner, it is unnecessary to use an organic transition metal complex which is generally difficult to dissolve or disperse in organic solvents and water and is possible to introduce even a transition metal easily through conversion to an acetylide, and therefore even a hard-to-dissolve transition metal compound is applicable to a coating composition without restraint. Further, the occurrence of an organic acid salt as an anion in the electrocoating bath, which is encountered when a transition metal organic acid salt is used, can be avoided and, furthermore, the metal ion will not be removed through ultrafiltration, hence the bath management and the design of

electrocoatings become easy.

The resin composition may contain a carbon-carbon double bond where desired. Since the above-mentioned carbon-carbon double bond has high reactivity, curability can be further enhanced.

Preferably, the content of the above-mentioned carbon-carbon double bond is within a range of 10 milli moles (lower limit) to 485 milli moles (upper limit), per 100 g of the solid matter in the resin composition provided that the total content of the propargyl group and carbon-carbon double bond conditions to be mentioned later are satisfied. When this content is less than 10 milli moles per 100 g of the solid matter, an improvement in curability by addition of the carbon-carbon double bond cannot be adequately exerted, and when it exceeds 485 milli moles per 100 g of the solid matter, the hydration stability in the case of being used as an electrocoating may be affected. As for the content of the carbon-carbon double bond, a more preferable content can be selected in accordance with the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the lower limit is preferably 20 milli moles and the upper limit is preferably 375 milli moles, per 100 g of the solid matter in the resin composition.

When the resin composition contains the above carbon-carbon double bond, the total content of the above propargyl group and the above carbon-carbon double bond is preferably within a range of 80 milli moles (lower limit) to 450 milli moles (upper limit), per 100 g of the solid matter in the above resin composition. When this content is less than 80 milli moles per 100 g of the solid matter, curability may become insufficient, and when it exceeds 450 milli moles per 100 g of the solid matter, the sulfonium group content becomes less and a dielectric breakdown voltage may become insufficient. As for the total content of the propargyl group and the carbon-carbon double bond, a more preferable content can be

selected in accordance with the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the lower limit is more preferably 100 milli moles and the upper limit is more preferably 395 milli moles, per 100 g of the solid matter in the resin composition.

In addition, when the resin composition contains the above carbon-carbon double bond, the total content of the sulfonium group, the propargyl group and the carbon-carbon double bond is preferably 500 milli moles or less per 100 g of the solid matter in the resin composition. When this content exceeds 500 milli moles per 100 g of the solid matter, a resin may not be attained in fact or a desired performance may not be attained. As for the total content of the sulfonium group, the propargyl group and the carbon-carbon double bond, a more preferable content can be selected in accordance with the resin skeleton employed. In the case of novolak phenol epoxy resins and novolak cresol epoxy resins, for example, the total content is more preferably 400 milli moles or less per 100 g of the solid matter in the resin composition.

The above resin composition can favorably be produced, for example, by the step (i) of reacting an epoxy resin having at least two epoxy groups in a molecule with a compound having a functional group capable of reacting with the epoxy group and a propargyl group to obtain an epoxy resin composition containing a propargyl group and the step (ii) of reacting the residual epoxy groups in the epoxy resin composition having a propargyl group(s) obtained in the step (i) with a sulfide/acid mixture to introduce the sulfonium group.

The above-mentioned compound having a functional group capable of reacting with the epoxy group and a propargyl group (hereinafter, referred to as "compound (A)") may be, for example, a compound having both a functional group capable of reacting with the epoxy group, such as a hydroxyl or carboxyl group, and a propargyl group. As specific examples, there may be given propargyl alcohol and propargylic acid. In particular,

propargyl alcohol is preferable from the viewpoint of its availability and good reactivity.

For providing the above resin composition with a carbon-carbon double bond as required, a compound having a functional group capable of reacting with the epoxy group and a carbon-carbon double bond (hereinafter, referred to as "compound (B)") may be used in combination with the compound (A) in the step (i). As the compound (B), a compound having both a functional group capable of reacting with the epoxy group, such as a hydroxyl or carboxyl group, and a carbon-carbon double bond may be used. Specifically, when the group capable of reacting with the epoxy group is a hydroxyl group, examples of the compound (B) may include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, allyl alcohol, methacrylic alcohol, and the like. When the group capable of reacting with the epoxy group is a carboxyl group, examples of the compound (B) may include acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, phthalic acid, itaconic acid; half esters such as maleic acid ethyl ester, fumaric acid ethyl ester, itaconic acid ethyl ester, succinic acid mono(meth)acryloyloxyethyl ester, and phthalic acid mono(meth)acryloyloxyethyl ester; synthetic unsaturated fatty acids such as oleic acid, linolic acid, ricinolic acid, and the like; and nature-derived unsaturated fatty acids such as linseed oil, soybean oil, and the like.

In the step (i), the epoxy resin having at least two epoxy groups in a molecule is reacted with the compound (A) to obtain an epoxy resin composition containing a propargyl group(s) or reacted with the compound (A) and the compound (B) as required to obtain an epoxy resin composition containing a propargyl group(s) and carbon-carbon double bond. In the latter case, in the step (i), the compound (A) and compound (B) may be mixed together in advance and then subjected to reaction, or the compound (A) and compound (B) may be separately subjected to

reaction. In addition, the functional group reacting with the epoxy group which the compound (A) has and the functional group reacting with the epoxy group which the compound (B) has may be the same or different.

5           When, in the step (i), the compound (A) and compound (B) are subjected to reaction with the epoxy resin, the portion between both compounds to be blended may be selected so as to attain the desired content of specified functional groups, for example, the above-mentioned contents of the propargyl group  
10 and carbon-carbon double bond.

          As for the reaction conditions in the step (i), the reaction is generally carried out at room temperature or 80 to 140°C for several hours. In addition, publicly known ingredients, which are required for the progress of the reaction, such as a catalyst  
15 and/or solvent may be used as required. The completion of the reaction can be checked by measuring an epoxy equivalent, and the functional group introduced can be identified by analysis of nonvolatile content and instrumental analysis of the resin composition obtained. The reaction product thus obtained  
20 generally occurs as a mixture of epoxy resins having one or more propargyl groups, or a mixture of epoxy resins having one or more propargyl groups and one or more carbon-carbon double bonds. In this sense, there can be obtained the resin composition having a propargyl group(s), or a propargyl group and carbon-carbon  
25 double bond through the step (i).

          In the step (ii), the residual epoxy groups in the epoxy resin composition containing a propargyl group, obtained in the step (i), are reacted with a sulfide/acid mixture to introduce a sulfonium group. This introduction of the sulfonium group  
30 can be effected by the method which comprises causing the sulfide/acid mixture to react with the epoxy group to conduct introduction of the sulfide and conversion thereof to the sulfonium group or the method which comprises introducing a sulfide and then converting the introduced sulfide to a sulfonium  
35 group with an acid, an alkyl halide such as methyl fluoride,

methyl chloride or methyl bromide, or the like, if necessary, followed by anion exchange. From the viewpoint of the availability of the reactant, the method using a sulfide/acid mixture is preferred.

5           The sulfide and acid are not particularly limited, and specifically, the above-mentioned substances can be given.

          The mixing ratio between the sulfide and acid in the above sulfide/acid mixture is generally and preferably about 100/40 to 100/100 as expressed in terms of sulfide/acid mole ratio.

10           The reaction in the step (ii) can be carried out, for example, by mixing the epoxy resin composition having a propargyl group, obtained in the step (i), and the above sulfide/acid mixture in an amount selected so as to give the above-mentioned sulfonium group content, for instance, with water in an amount of 5 to  
15 10 moles per mole of the sulfide used and stirring the mixture generally at 50 to 90°C for several hours. A residual acid value of 5 or less may serve as a criterion in determining the reaction to be completed. The introduction of sulfonium group in the resin composition obtained can be identified by potentiometric  
20 titration.

          The same procedure can be used also in the case where the sulfide is first introduced and then converted to the sulfonium group. By introducing the sulfonium group after introduction of the propargyl group, as described above, the sulfonium group  
25 can be prevented from being decomposed due to heating.

          In the case of converting part of the propargyl group in the above resin composition to an acetylide, the conversion to the acetylide can be carried out by the step of reacting the epoxy resin composition, containing a propargyl group, obtained  
30 in the step (i) with a metal compound to thereby convert part of the propargyl group in the above epoxy resin composition to the corresponding acetylide. The above-mentioned metal compound is preferably a transition metal compound capable of giving an acetylide, and examples thereof may include complexes  
35 or salts of such transition metals as copper, silver and barium.



Specific examples thereof may include acetylacetonato-copper, copper acetate, acetylacetonato-silver, silver acetate, silver nitrate, acetylacetonato-barium, and barium acetate. In particular, copper or silver compounds are preferable from the viewpoint of the conformity with an environment, and copper compounds are more preferable because of their ready availability. For example, acetylacetonato-copper is suitably used in view of the ease of bath control.

As for the reaction conditions of converting part of the propargyl group to an acetylide, the reaction is generally carried out at 40 to 70°C for several hours. The progress of the reaction can be checked by the coloration of the resulting resin composition and/or the disappearance of the methine proton signal on a nuclear magnetic resonance spectrum. Thus, the time when the propargyl group-derived acetylide in the resin composition arrives at a desired level is determined and, at that time, the reaction is terminated. The reaction product obtained is generally a mixture of epoxy resins with one or more propargyl groups converted to an acetylide. A sulfonium group can be introduced, by the step (ii), into the thus obtained epoxy resin composition with part of the propargyl group converted to an acetylide.

The step of converting part of the propargyl group in the epoxy resin composition to an acetylide and the step (ii) can be carried out under common reaction conditions, so that both steps can be carried out simultaneously. The method of carrying out both steps simultaneously can advantageously simplify the production process.

In this way, the resin composition containing a propargyl group and a sulfonium group, and optionally containing a carbon-carbon double bond and/or a propargyl group-derived acetylide as required can be produced while preventing the sulfonium group from being decomposed. Incidentally, acetylides in a dry state are explosive but the reaction is carried out in an aqueous medium and the desired substance can be obtained

in the form of an aqueous composition. Therefore, there arises no safety problem.

Since the cationic electrocoating comprises the resin composition and the resin composition itself is curable, it is not always necessary to use a curing agent. However, for further improving the curability, a curing agent may be used. Examples of the curing agent may include compounds having a plurality of at least one species of propargyl groups and carbon-carbon double bonds, for example compounds obtained by adding a compound containing a propargyl group, such as propargyl alcohol, or a compound, containing carbon-carbon double bond, such as acrylic acid to polyepoxide such as a novolak phenol or pentaerythritol tetraglycidyl ether.

It is not always necessary to use a curing catalyst in the cationic electrocoating. However, when a further improvement in curability is required depending on the curing reaction conditions, a transition metal compound in general use may be appropriately added as required. Such compound is not particularly limited, and examples thereof may include complexes or compounds formed by combining a ligand, such as cyclopentadiene or acetylacetone, or a carboxylic acid such as acetic acid, with transition metals such as nickel, cobalt, manganese, palladium and rhodium. The amount of the above curing catalyst to be added is preferably from 0.1 milli mole (lower limit) to 20 milli moles (upper limit) per 100 g of the resin solid matter in the cationic electrocoating.

An amine may further be blended in the cationic electrocoating. By the addition of the amine, the conversion of the sulfonium group to a sulfide by electrolytic reduction in the process of electrodeposition is increased. The amine is not particularly limited, and examples thereof may include amine compounds such as primary to tertiary monofunctional or polyfunctional aliphatic amines, alicyclic amines and aromatic amines. In particular, water-soluble or water-dispersible ones are preferable. Examples of the amines may include alkylamines

having 2 to 8 carbon atoms such as monomethylamine, dimethylamine, trimethylamine, triethylamine, propylamine, diisopropylamine and tributylamine; monoethanolamine, dimethanolamine, methylethanolamine, dimethylethanolamine, cyclohexylamine, morpholine, N-methylmorpholine, pyridine, pyrazine, piperidine, imidazoline, imidazole and the like. These may be used alone or two or more of them may be used in combination. In particular, hydroxy amines such as monoethanolamine, diethanolamine and dimethylethanolamine are preferred from the view point of excellent dispersion stability in water.

The above amine can be directly blended in the cationic electrocoating. While in the conventional neutralized amine type electrocoating, the addition of a free amine results in deprivation of the neutralizing acid in the resin, hence in marked deterioration of the stability of the electrocoating solution, no such bath stability trouble will arise in the present invention.

The amount of the above amine to be added is preferably 0.3 meq (lower limit) to 25 meq (upper limit) per 100 g of the resin solid matter in the cationic electrocoating. When this amount is less than 0.3 meq per 100 g, the film thickness retention may become insufficient. When it exceeds 25 meq per 100 g, the effects proportional to the addition amount can no longer be obtained; this is not economical. The lower limit is more preferably 1 meq per 100 g, and the upper limit is more preferably 15 meq per 100 g.

In the cationic electrocoating, there may also be incorporated an aliphatic hydrocarbon group-containing resin composition. The incorporation of the aliphatic hydrocarbon group-containing resin composition results in an improvement in the shock resistance of the coating films obtained. As the aliphatic hydrocarbon group-containing resin composition, there may be mentioned those containing, per 100 g of the solid matter in the resin composition, 5 to 400 millimoles of a sulfonium group, 80 to 135 milli moles of an aliphatic hydrocarbon group

containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in the chain thereof and 10 to 315 milli moles of at least one of a propargyl group and organic groups containing 3 to 7 carbon atoms and having a terminal unsaturated  
5 double bond on condition that the total content of the sulfonium group, the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in the chain thereof and the propargyl group and organic groups containing 3 to 7 carbon atoms and having a terminal unsaturated  
10 double bond is not more than 500 milli moles per 100 g of the solid matter in the resin composition.

When such an aliphatic hydrocarbon group-containing resin composition is incorporated in the above cationic electrocoating, the resin solid matter in the cationic electrocoating preferably  
15 contains, per 100 g thereof, 5 to 400 milli moles of sulfonium group, 10 to 300 milli moles of the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in the chain thereof and a total of 10 to 485 milli moles of the propargyl group and organic groups  
20 containing 3 to 7 carbon atoms and having a terminal unsaturated double bond, and the total content of the sulfonium group, the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in the chain thereof, the propargyl group and the organic groups containing  
25 3 to 7 carbon atoms and having a terminal unsaturated double bond is not more than 500 milli moles per 100 g of the resin solid matter in the cationic electrocoating, and the content of the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in  
30 the chain thereof is 3 to 30% by weight relative to the resin solid matter in the electrocoating.

When the aliphatic hydrocarbon group-containing resin composition is incorporated in the above cationic electrocoating and the sulfonium group content level is lower than 5 milli moles  
35 per 100 g, any satisfactory curability cannot be attained and,

further, the hydratability and bath stability will be poor. When it exceeds 400 milli moles per 100 g, the deposition of films on the surface of the substrate becomes poor. When the content of the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally containing an unsaturated double bond in the chain thereof is less than 80 milli moles per 100 g, the shock resistance will not be improved to a satisfactory extent and, when it exceeds 350 milli moles per 100 g, the resin composition becomes difficult to handle. When the total content of the propargyl group and the organic groups containing 3 to 7 carbon atoms and having a terminal unsaturated double bond is less than 10 milli moles per 100 g, no satisfactory curability can be manifested on the occasion of combined use of another resin and/or another curing agent and, when it exceeds 315 milli moles per 100 g, the shock resistance will not be improved to a satisfactory extent. The total content of the sulfonium group, the aliphatic hydrocarbon group containing 8 to 24 carbon atoms and optionally having an unsaturated double bond in the chain thereof, the propargyl group and the organic groups containing 3 to 7 carbon atoms and having a terminal unsaturated double bond is not more than 500 milli moles per 100 g of the solid matter in the resin composition. When it exceeds 500 milli moles, any corresponding resin cannot be obtained in actuality or the desired performance characteristics cannot be obtained in some instances.

The above-mentioned cationic electrocoating may further contain another components used in an ordinary cationic electrocoating as required. The above-mentioned another component is not particularly limited, and examples thereof may include a pigment, a rust preventive, a pigment dispersion resin, a surfactant, an antioxidant and an ultraviolet absorber. However, when the above-mentioned components are used, it is preferred to adjust the amount of the component to be blended paying attention to the retention of a dielectric breakdown voltage.

The pigment is not particularly limited, and examples thereof may include coloring pigments such as titanium dioxide, carbon black and red iron oxide; rust-preventive pigments such as basic lead silicate and aluminum phosphomolybdate; and  
5 extender pigments such as kaoline, clay and talc. Examples of the rust preventive, specifically, may include calcium phosphite, zinc calcium phosphite, calcium-carrying silica, calcium-carrying zeolite, and the like. The total amount of the above-mentioned pigments and rust preventives to be added  
10 is preferably 0 % by weight (lower limit) to 50 % by weight (upper limit) in terms of the solid matter in the cationic electrocoating.

The pigment dispersion resins are used to stably disperse the pigments in the cationic electrocoating. The pigment  
15 dispersion resins are not particularly restricted but include those pigment dispersion resins which are in general use. A pigment dispersion resin containing a sulfonium group and an unsaturated bond within the resin may also be used. Such pigment dispersion resin containing a sulfonium group and an unsaturated  
20 bond can be obtained, for example, by the method comprising reacting a sulfide compound with a hydrophobic epoxy resin obtained by reacting a bisphenol-based epoxy resin with a half-blocked isocyanate, or reacting the resin with a sulfide compound in the presence of a monobasic acid and a hydroxyl  
25 group-containing dibasic acid. The pigment dispersion resins can also stably disperse the rust preventives containing no heavy metal in the cationic electrocoating.

The cationic electrocoating can be prepared, for example, by admixing the resin composition with the above-mentioned other  
30 ingredients as required and dissolving or dispersing the resulting composition in water. On the occasion of use in the electrodeposition step, the bath solution/dispersion prepared preferably has a nonvolatile matter content of 5 % by weight (lower limit) to 40 % by weight (upper limit). The preparation  
35 is preferably carried out in such a way that the contents of

the propargyl group, carbon-carbon double bond and sulfonium group in the electrocoating may not deviate from the respective ranges indicated above referring to the resin composition.

In the method of coating a square wire of the present invention, the electrodeposition can be carried out using an electrodeposition apparatus in which the conventional cationic electrodeposition can be carried out. For example, the electrodeposition can be carried out using a cationic electrodeposition apparatus for electric wire which comprises an electrodeposition means, a washing means, and a heating means combined in that order. In this way, insulated wires having the high dielectric breakdown voltage can be obtained in an efficient manner.

The above-mentioned electrodeposition means is aimed to form a film on the surface of an electric wire being a article to be coated by cationic electrodeposition using a cationic electrocoating. The electrodeposition means is not particularly limited as long as it is one capable of conducting cationic electrodeposition.

In operating the electrodeposition means, the method comprising, for example, immersing an article to be coated in the cationic electrocoating for utilizing the article as a cathode, and applying a voltage generally within the range of 50 to 450 V between the cathode and an anode may be given as an example. When the voltage applied is lower than 50 V, the dielectric breakdown voltage may be possibly lowered and insufficient electrodeposition will result. When it exceeds 450 V, the electricity consumption uneconomically increases. When the cationic electrocoating is used and a voltage within the range is applied, a uniform film can be formed on the whole material surface without any rapid increase in film thickness in the process of electrodeposition. In ordinary cases, a bath temperature of the cationic electrocoating in applying the above voltage is preferably 10 to 45°C.

The above-mentioned washing means is intended for washing

the article with the cationic electrocoating adhering thereto to remove the electrocoating bath liquid. The washing means is not particularly restricted but may be any the conventional washing apparatus. For example, there may be given an apparatus  
5 in which the electrodeposited article is washed using, as a washing liquid, the filtrate obtained by ultrafiltration of the electrocoating bath liquid. As the above-mentioned heating means, there may be specifically given a hot air drying oven, a near-infrared heating oven, a far-infrared heating oven, and  
10 an induction heating oven, for instance.

The article to be coated (square wire), to which the method of coating a square wire in accordance with the present invention is applicable, is not particularly limited as long as it is one which exhibits conductivity by which cationic electrodeposition  
15 can be conducted, and examples thereof may include electric wires consisting of metals such as iron, copper, aluminum, gold, silver, nickel, tin, zinc, titanium and tungsten, and alloys containing these metals. In particular, an electric wire consisting of copper, gold, aluminum, iron or an alloy based on these metals  
20 is preferable.

The above-mentioned method of coating a square wire is favorably applicable to coating of a square wire and can also be favorably applied particularly to coating of an electric wire having a small curvature of the edges in the cross-sectional  
25 profile, which is considered to be difficult to coating. In addition, the curvature used in this description refers to one, which is represented by (a radius of a curve of the edge/a length of one side)  $\times$  100 in a cross section of the electric wire. When the method of coating a square wire in accordance with the present  
30 invention is applied to an article to be coated, having a curvature of the edges of 1 to 20%, an insulated wire of a square wire, according to the metal foil method of JIS C 3003 and having a dielectric breakdown voltage of 2 kV or higher, can be attained.

The insulated wire of a square wire obtained by the  
35 above-mentioned method of coating a square wire is one in which



a sufficient insulating film is formed throughout the whole surface of the square wire, that is, the whole surface including the edges and the dielectric breakdown voltage is further enhanced. Therefore, the insulated wire of a square wire  
5 obtained by this coating method can be favorably used as an electric wire having a high dielectric breakdown voltage. Moreover, since the insulated wire of a square wire is less susceptible of changes in the shape during the manufacturing processes, the occupancy ratio possessed by the square wire can  
10 be maintained, with the result that the occupancy ratio of the resulting insulated wire is improved. Consequently, in comparison with cases in which a round wire with the same volume is used, it is possible to further improve the performances. Such the insulated wire, too, constitutes an aspect of the present  
15 invention.

Moreover, the present invention is also a method of coating a square wire comprising a step (I) of forming a first insulating film by cationic electrodeposition using a cationic electrocoating, and a step (II) of forming a second insulating  
20 film on the first insulating film formed in the step (I) using an insulating coating, said cationic electrocoating containing a resin composition of which a hydratable functional group is reduced directly by an electron and passivated, resulting in deposition of a film and the cationic electrocoating and/or the  
25 insulating coating containing crosslinked resin particles.

In other words, in a second method of coating a square wire, by forming a first insulating film by cationic electrodeposition using a cationic electrocoating containing a resin composition of which a hydratable functional group is  
30 reduced directly by an electron and passivated, resulting in deposition of a film and forming a second insulating film on the first insulating film using an insulating coating formed by containing polyvinyl formal resin, polyurethane resin, polyester resin, polyamide resin, polyester imide resin,  
35 polyamideimide resin, polyimide resin resin, or epoxy resin or

the like, an insulated wire of a square wire having a higher dielectric breakdown voltage than that of an insulated wire formed by applying only the cationic electrocoating or only the insulating coating, can be attained.

5           In the process for obtaining an insulated wire of a square wire by coating and curing the previous insulating coating, an insulated wire is prepared by repeating a cycle of coating and curing of an insulating coating usually around 7 to 15 times. Since the insulating property can be improved by repeating a  
10   cycle of coating and curing, it is necessary to repeat the cycle many times in order to obtain the desired insulating property. To the contrary, in the method of coating a square wire, by applying an insulating coating, preferably repeating a cycle of applying an insulating coating around several times after the step (I),  
15   an insulated wire of a square wire having a high dielectric breakdown voltage can be obtained and, therefore, the number of steps can be reduced, and the manufacturing cost can be also reduced.

Moreover, in the second method of coating a square wire,  
20   the above-mentioned cationic electrocoating and/or insulating coating are allowed to contain crosslinked resin particles. That is, in the second method of coating a square wire, crosslinked resin particles are contained in at least either one of the cationic electrodeposition coating used in process (I) and the  
25   insulating coating used in process (II). The crosslinked resin particle has the function of providing a thixotropic property in the coating. Thus, an insulating film can be formed in a sufficient film thickness even at edges of an article to be coated (a square wire), and, as a result, an insulated wire of a square  
30   wire having a high dielectric breakdown voltage can be attained.

For example, when the step (I) is performed using the cationic electrocoating containing the crosslinked resin particles, the function of the crosslinked resin particle to provide a thixotropic property allows the whole surface of the  
35   article to be coated (a square wire), that is, the whole surface

including the edges of a square wire to be coated with a sufficient insulating film and an insulated wire of a square wire to be obtained to be provided with a high dielectric breakdown voltage. In addition, also when the step (II) is performed using the  
5 insulating coating containing crosslinked resin particles, a second insulating film with a sufficient film thickness is formed at edges, and an insulated wire having a high dielectric breakdown voltage can be obtained. Since the crosslinked resin particle imparts such the function, when the step (I) is performed using  
10 the cationic electrocoating containing crosslinked resin particles, and the step (II) is performed using the insulating coating containing crosslinked resin particles, at not only flat portions and but also edges of an article (a square wire), coating with a first insulating film and a second insulating film is  
15 sufficiently done, and as a result, a dielectric breakdown voltage of the resulting insulated wire of a square wire can be made higher. Therefore, from a viewpoint that the resulting insulated wire of a square wire has a higher dielectric breakdown voltage, it is preferable to employ each coating containing  
20 crosslinked resin particles in both of the step (I) and the step (II). In addition, when the case of use of crosslinked resin particle only in the step (I) and the case only in the step (II) are compared, it is preferable to use only in the step (I) from a viewpoint that the resulting insulated wire of a square wire  
25 has a higher dielectric breakdown voltage.

In the same manner as the first invention, in the coating process by using the cationic electrocoating, the shifting speed of the square wire in the electrocoating bath is set in a range from 1 to 80 m/min, and the shortest distance from the  
30 liquid-contact portion of the square wire onto the cationic electrocoating to the electrode is set longer than 1/2 of the total shift distance of the square wire from the liquid-contact portion of the square wire to the liquid-separation portion in the electrocoating bath.

35 Fig. 5 shows an example of a conceptual view of a cross

section of the insulated wire of a square wire obtained by performing the step (I) using a cationic electrocoating containing crosslinked resin particles and performing the step (II) using an insulating coating containing crosslinked resin particles in the second method of coating a square wire. Fig. 5 shows an insulated wire of a square wire 10, which is obtained by forming a first insulating film 8, to be formed by electrodeposition using the cationic electrocoating, and a second insulating film 9, to be formed by applying the insulating coating on a square wire 7. The insulated wire of a square wire 10, obtained in the case where coatings containing the crosslinked resin particles are used in the step (I) and the step (II), is provided with the first insulating film 8 and the second insulating film 9 with a sufficient film thickness on flat portions 13 and even on edges 11 of the square wire 7. Accordingly, the insulated wire of a square wire 10 obtained by the above coating method has a high dielectric breakdown voltage.

On the other hand, Fig. 6 shows an example of a conceptual view of a cross section of the insulated wire obtained by forming a first insulating film using a cationic electrocoating containing no crosslinked resin particles and forming a second insulating film using an insulating coating containing no crosslinked resin particles. The insulated wire of a square wire 12, obtained in the case where coatings containing no crosslinked resin particles are used, is provided with the first insulating film 8 and the second insulating film 9 with a sufficient film thickness on flat portions 13 of the square wire 7, but not provided with the first insulating film 8 and the second insulating film 9 with a sufficient film thickness on the edges 11 of the square wire 7. Consequently, the insulated wire of a square wire 12 obtained by using this coating method has a lower dielectric breakdown voltage in comparison to the insulated wire obtained by the method of coating a square wire in accordance with the present invention.

The crosslinked resin particle is not particularly limited, but includes crosslinked resin particles described above.

Preferably, the crosslinked resin particle is one of which a hydratable functional group is reduced directly by electrons and passivated.

Preferably, the content of the crosslinked resin particles is 0.5 to 40 % by weight in the coating.

Preferably, the crosslinked resin particle is obtained by emulsion polymerizing an  $\alpha, \beta$ -ethylenically unsaturated monomer mixture using a resin having an onium group as an emulsifier.

Preferably, the resin having an onium group has 2 to 15 onium groups per one molecule.

Preferably, the emulsifier is an acrylic resin or an epoxy resin.

Preferably, the onium group is an ammonium group or a sulfonium group.

Preferably, the acrylic resin or the epoxy resin, having the ammonium group or the sulfonium group, is obtained by adding a tertiary amine compound or sulfide and an organic acid to an acrylic resin or an epoxy resin, having an epoxy group, to convert the acrylic resin or the epoxy resin to a quaternary ammonium compound or a tertiary sulfonium compound.

Preferably, a number-average molecular weight of the acrylic resin or the epoxy resin, having an epoxy group, is 2000 to 20000.

The above-mentioned cationic electrocoating is not particularly limited, but includes cationic electrocoatings described above.

Preferably, the cationic electrocoating contains crosslinked resin particles.

Preferably, the resin composition has a sulfonium group and a propargyl group.

Preferably, the resin composition has a sulfonium group content of 5 to 400 milli moles, a propargyl group content of

10 to 495 milli moles and a total content of the sulfonium and propargyl groups of 500 milli moles or less, per 100 g of the solid matter in the resin composition.

Preferably, the resin composition includes an epoxy resin  
5 having a novolak cresol epoxy resin or a novolak phenol epoxy resin as a skeleton and having a number-average molecular weight of 700 to 5000, and the resin composition also has a sulfonium group content of 5 to 250 milli moles, a propargyl group content of 20 to 395 milli  
10 moles and a total content of the sulfonium and propargyl groups of 400 milli moles or less, per 100 g of the solid matter in the resin composition.

In the second method of coating a square wire of the present invention, The insulating coating is not particularly limited  
15 as long as it is a coating capable of forming an insulating film having a high dielectric breakdown voltage, and examples thereof may include various conventionally known insulating coatings formed by containing organic resins such as polyvinyl formal resin, polyamide resin, polyimide resin, polyamide-imide resin,  
20 polyester-imide resin, polyester resin, polyurethane resin and epoxy resin.

Examples of an insulating coating formed by containing the above-mentioned polyvinyl formal resin may include a coating containing a polyvinyl formal resin and a phenol resin and, as  
25 a commercially available product, PVFS7-24 (made by Totoku Toryo Co., Ltd.) and the like are suitably used.

Examples of an insulating coating formed by containing the above-mentioned polyamide resin may include aramid (total aromatic polyamide) coatings, nylon MXD 6 coatings and the like.  
30 In particular, aramid coatings are preferred in point of heat resistance, mechanical strength and the like.

Examples of an insulating coating formed by containing the above-mentioned polyimide resin may include total aromatic polyimide coatings and the like and, as a commercially available  
35 product, Pyre-ML (product name, made by DuPont K.K.), TORAYNEECE

3000 (product name, made by Toray Industries, Inc.) and the like are suitably used.

Examples of an insulating coating formed by containing the above-mentioned polyamide-imide resin may include a coating prepared by reacting tricarboxylic anhydride with diisocyanate, and the like and, as a commercially available product, NEOHEAT AI (made by Totoku Toryo Co., Ltd.) and the like are given.

Examples of an insulating coating formed by containing the above-mentioned polyester-imide resin may include a coating prepared by further reacting imide-dicarboxylic acid, which is a reaction product of tricarboxylic anhydride and diamine, with a polyhydric alcohol and, as a commercially available product, NEOHEAT 8600A (made by Totoku Toryo Co., Ltd.) and the like are given.

Examples of an insulating coating formed by containing the above-mentioned polyester resin may include alkyd resin coatings, especially, glycerine-modified alkyd resin coatings, tris(hydroxyethyl)isocyanurate (THEIC)-modified alkyd resin coatings, and the like and, as a commercially available product, NEOHEAT 8200K1 (made by Totoku Toryo Co., Ltd.) and the like are given.

Examples of an insulating coating formed by containing the above-mentioned polyurethane resin may include a coating prepared by reacting diisocyanate with a polyester resin, and the like and, as a commercially available product, TPU F1 (made by Totoku Toryo Co., Ltd.) and the like are given.

Examples of an insulating coating formed by containing the above-mentioned epoxy resin may include a coating containing a bisphenol A type epoxy resin and a phenolic resin, and the like and, as a commercially available product, CEMEDINE 110 (made by CEMEDINE Co., Ltd.) and the like are given. Among the insulating coatings described above, the insulating coating formed by containing the above-mentioned polyamide-imide resin is preferred in that the obtained insulating wire of a square wire has a higher dielectric breakdown voltage.

When the insulating coating containing the crosslinked resin particle is used, the content of the crosslinked resin particle is preferably in an amount of 0.5 to 40 % by weight relative to the resin solid matter in the coating composition.

5 When the above-mentioned content of the crosslinked resin particle is less than 0.5 % by weight, the thickness of film at the edges may become insufficient, and when it exceeds 40 % by weight, an appearance of the insulating film may be deteriorated. The above content is more preferably 1 to 30 %  
10 by weight.

In addition, in the case where the insulating coating composition of the present invention is used in the form of an organic solvent, the crosslinked resin particle obtained by the above-mentioned NAD method can be contained in the insulating  
15 coating composition as it is, but when the crosslinked resin particle is obtained by the above-mentioned emulsion method, a crosslinked resin particle, obtained by eliminating water content through substituting a solvent for, azeotropically distilling, centrifuging, filtering or drying the obtained  
20 crosslinked resin particle to convert the crosslinked resin particle to an organic solvent type, can be contained in the insulating coating composition.

In the second method of coating a square wire, the step (II) can be performed by a conventionally known method such as  
25 an application and baking of the above-mentioned insulating coating. As a method of applying the above-mentioned insulating coating, a dice technique and a felt technique are conventionally well known.

The present invention relates to A method of coating a  
30 square wire comprising a step of:

carrying out cationic electrodeposition on a square wire to form an insulating film thereon, by using a cationic electrocoating that stored in an electrocoating bath, wherein the cationic electrocoating contains a resin composition of which  
35 a hydratable functional group is reduced directly by electrons



and passivated, resulting in deposition of a film, and the cationic electrocoating contains crosslinked resin particles. In other words, in the above-mentioned method of coating a square wire, the cationic electrocoating is allowed to contain the crosslinked resin particles so that an insulating film is sufficiently formed not only on flat portions of the square wire, but also on the edges thereof.

Therefore, the application of the method of coating a square wire of the present invention makes it possible to obtain an insulated wire of a square wire having a high dielectric breakdown voltage. In particular, when the resin composition contains a sulfonium group and a propargyl group, it is possible to obtain an insulated wire of a square wire having a higher dielectric breakdown voltage.

Moreover, since the resulting insulated wire of a square wire is allowed to have a higher occupancy ratio, the performances are improved in comparison with the application of a round wire having the same volume. Therefore, the insulated wire of a square wire, obtained by the method of coating a square wire of the present invention, can be desirably used in various applications as an insulated wire with a high dielectric breakdown voltage.

Furthermore, since a roll wire derived from the insulated wire of a square wire has a high occupancy ratio, it becomes possible to form a greater cross-sectional area of the electric wire, and consequently to allow application for a high electric current. Moreover, since adjacent wound electric wires are made in face-contact with each other, it is possible to improve heat releasing property, and also to reduce electric resistance. Therefore, the performance thereof can be enhanced and the size and the weight can be reduced so that a greater magnetomotive force is obtained. The above-mentioned roll wire is applicable to various coils such as solenoid coils and toroidal coils.

The method for obtaining a roll wire from the insulated wire of a square wire is not particularly limited, but includes a method in which an insulated wire is wound around a coil former

manually or by using a wire-winding device, while applying a bonding agent thereto, if necessary and so on.

By using the method of coating a square wire comprising the above-mentioned steps (I) and (II), it becomes possible to  
5 provide an insulated wire that has a higher dielectric breakdown voltage and can be used for various applications.

Moreover, the roll wire obtained from such an insulated wire also has a high occupancy ratio and makes it possible to increase the cross-sectional area of the electric wire; therefore,  
10 the roll wire can be used under a large current, and is consequently utilized as various coils such as solenoid coils and toroidal coils.

#### EXAMPLES

15 Hereinafter, the present invention will be described more specifically by way of examples, but the present invention is not limited to these examples. In the examples, "part(s)" means "part(s) by weight", and "%" means "% by weight", unless otherwise specified.

20

##### Production Example 1

Production of an acrylic resin 1 having an epoxy group

Butyl cellosolve (120 parts) was put in a reaction container and heated under stirring at 120°C. A mixed solution  
25 of 2 parts of tert-butylperoxy-2-ethylhexanoate and 10 parts of butyl cellosolve, and a monomer mixture consisting of 40 parts of glycidyl methacrylate, 150 parts of 2-ethylhexyl methacrylate, 50 parts of 2-hydroxyethyl methacrylate and 65 parts of n-butyl methacrylate were added dropwise thereto over 3 hours. This  
30 mixture was aged for 30 minutes and, then, a mixed solution of 0.5 part of tert-butylperoxy-2-ethylhexanoate and 5 parts of butyl cellosolve was added dropwise thereto over 30 minutes. Further, the resulting mixture was aged for 2 hours to obtain the solution of an acrylic resin 1 having an epoxy group with  
35 a non-volatile content of 42%. The number-average molecular

weight, measured by gel permeation chromatography (GPC) in terms of polystyrene, of this acrylic resin 1 having an epoxy group was 11000.

## 5 Production Example 2

Production of an ammonium quaternizing agent 1

Isophorone diisocyanate (220 parts), 40 parts of methyl isobutyl ketone and 0.22 part of dibutyltin dilaurate were put in a reaction container, and 135 parts of 2-ethylhexanol was  
10 added dropwise thereto at 55°C. Thereafter, the mixture was reacted at 60°C for 1 hour to obtain a half-blocked isocyanate solution. This solution was further heated to 80°C and a mixed solution of 90 parts of N,N-dimethylaminoethanol and 10 parts of methyl isobutyl ketone was added dropwise thereto over 30  
15 minutes. After recognizing that an isocyanate group disappeared using infrared spectrum analysis, the mixed solution was cooled to room temperature to obtain tertiary amine having a blocked isocyanate group. This solution was neutralized by adding 180 parts of a 50% aqueous solution of lactic acid to  
20 obtain a solution of an ammonium quaternizing agent 1.

## Production Example 3

Production of an ammonium quaternizing agent 2

A solution of an ammonium quaternizing agent 1 was obtained  
25 by following the same procedure as in Production Example 2 except for using 160 parts of triethylene glycol monomethyl ether in place of 135 parts of 2-ethylhexanol used as a block agent and changing the amount of methyl isobutyl ketone as a solvent from 40 parts to 25 parts.

30

## Production Example 4

Production of an acrylic resin 1 having an ammonium group

120 parts of butyl cellosolve was put in a reaction container and heated under stirring at 120°C. A mixed solution  
35 of 2 parts of tert-butylperoxy-2-ethylhexanoate and 10 parts

of butyl cellosolve, and a monomer mixture, consisting of 15 parts of glycidyl methacrylate, 50 parts of 2-ethylhexyl methacrylate, 40 parts of 2-hydroxyethyl methacrylate and 15 parts of n-butyl methacrylate were added thereto in a dropwise manner over 3 hours. This mixture was aged for 30 minutes and, then, a mixed solution of 0.5 part of tert-butylperoxy-2-ethylhexanoate and 5 parts of butyl cellosolve was added thereto in a dropwise manner over 30 minutes. The resulting mixture was further aged for 2 hours and cooled.

10 This acrylic resin 2 having an epoxy group had the number-average molecular weight of 12,000 and the weight-average molecular weight of 28000, measured by GPC. By adding 7 parts of N,N-dimethylaminoethanol and 15 parts of a 50% aqueous solution of lactic acid to this acrylic resin 2 and heating under stirring

15 at 80°C, the acrylic resin 2 was quaternized. Heating was stopped at the time when an acid value reached 1 or less and a viscosity rise stopped to obtain the solution of an acrylic resin 1 with a nonvolatile content of 30% having an ammonium group. The number of ammonium groups per one molecule of this acrylic resin 1 having

20 an ammonium group was 6.0.

#### Production Example 5

Production of an acrylic resin 2 having an ammonium group

By adding 100 parts of the solution of the ammonium quaternizing agent 1 produced in Production Example 2 to 240 parts of the acrylic resin 1 having an epoxy group produced in Production Example 1 and heating under stirring at 80°C, the mixture was quaternized. Heating was stopped at the point in time when an acid value reached 1 or less and a viscosity rise

25 was not recognized to obtain the solution of an acrylic resin 2 having an ammonium group with a non-volatile content of 39%. The number of ammonium groups per a molecule of this acrylic resin 2 having an ammonium group was 8.5.

#### 35 Production Example 6

Production of an acrylic resin 3 having an ammonium group

The solution of an acrylic resin 3 having an ammonium group with a non-volatile content of 36% was obtained by following the same procedure as in Production Example 5 except for using 80 parts of the solution of the ammonium quaternizing agent 2 produced in Production Example 3 in place of 100 parts of the solution of the ammonium quaternizing agent 1. The number of ammonium groups per a molecule of this acrylic resin 3 having an ammonium group was 4.0.

10

Production Example 7

Production of a crosslinked resin particle 1

In a reaction container, 20 parts of the acrylic resin 1 having an ammonium group, produced in Production Examples 4, and 270 parts of ion-exchanged water were put, and the mixture was heated under stirring at 75°C. An aqueous solution of 1.5 parts of 2,2'-azobis(2-(2-imidazoline-2-yl)propane) neutralized wholly with acetic acid was added dropwise thereto over 5 minutes. The mixed solution was aged for 5 minutes and, then, 30 parts of methyl methacrylate was added dropwise thereto over 5 minutes. The mixture was further aged for 5 minutes, and preemulsion, which was obtained by adding an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture consisting of 170 parts of methyl methacrylate, 40 parts of styrene, 30 parts of n-butyl methacrylate, 5 parts of glycidyl methacrylate and 30 parts of neopentyl glycol dimethacrylate to a mixed solution of 70 parts of the acrylic resin 1 having an ammonium group and 250 parts of ion-exchanged water under stirring, was added dropwise thereto over 40 minutes. This mixture was aged for 60 minutes and, then, cooled to obtain a dispersion of a crosslinked resin particle 1. The resulting aqueous dispersion of the crosslinked resin particle 1 had a non-volatile content of 35%, a pH of 5.0 and a volume-average particle diameter of 100 nm. The aqueous dispersion of the crosslinked resin particle 1 was mixed with xylene to form a mixture and xylene was substituted

for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a crosslinked resin particle 1 in xylene.

#### 5 Production Example 8

##### Production of a crosslinked resin particle 2

In a reaction container, 20 parts of the acrylic resin 2 having an ammonium group, produced in Production Examples 5, and 300 parts of ion-exchanged water were put, and the mixture  
10 was heated under stirring at 75°C. An aqueous solution of 1 part of 2,2'-azobis(2-(2-imidazoline-2-yl)propane) neutralized wholly with acetic acid was added dropwise thereto over 5 minutes. The mixed solution was aged for 5 minutes and, then, 25 parts of methyl methacrylate was added dropwise thereto  
15 over 5 minutes. The mixture was further aged for 5 minutes and, then, preemulsion, which was obtained by adding an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture consisting of 140 parts of methyl methacrylate, 30 parts of styrene, 25 parts of n-butyl methacrylate, 5 parts of glycidyl methacrylate and 25  
20 parts of neopentyl glycol dimethacrylate to a mixed solution of 55 parts of the acrylic resin 2 having an ammonium group and 270 parts of ion-exchanged water under stirring, was added dropwise thereto over 40 minutes. This mixture was aged for 60 minutes and, then, cooled to obtain a dispersion of a  
25 crosslinked resin particle 2. The resulting aqueous dispersion of the crosslinked resin particle 2 had a non-volatile content of 30%, a pH of 5.5 and a volume-average particle diameter of 100 nm. The aqueous dispersion of the crosslinked resin particle 2 was mixed with xylene to form a mixture and xylene was substituted  
30 for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a crosslinked resin particle 2 in xylene.

#### Production Example 9

##### 35 Production of a crosslinked resin particle 3

An aqueous dispersion of a crosslinked resin particle 3 was obtained by following the same procedure as in Production Example 8 except that in place of the acrylic resin 2 having an ammonium group used as an emulsifier, the same amount of the acrylic resin 3 having an ammonium group was used. The resulting aqueous dispersion of the crosslinked resin particle 3 had a non-volatile content of 30 %, a pH of 5.5 and a volume-average particle diameter of 90 nm. The aqueous dispersion of the crosslinked resin particle 3 was mixed with xylene to form a mixture and xylene was substituted for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a crosslinked resin particle 3 in xylene.

#### 15 Production Example 10

Production of a crosslinked resin particle 4

An aqueous dispersion of a crosslinked resin particle 4 was obtained by following the same procedure as in Production Example 8 except for changing the amount of neopentyl glycol dimethacrylate in the  $\alpha,\beta$ -ethylenically unsaturated monomer mixture from 25 parts to 40 parts. The resulting aqueous dispersion of the crosslinked resin particle 4 had a non-volatile content of 30%, a pH of 5.0 and a volume-average particle diameter of 150 nm. This aqueous dispersion was mixed with xylene to form a mixture and xylene was substituted for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a crosslinked resin particle 4 in xylene.

#### 30 Production Example 11

Production of a crosslinked resin particle 5 using an emulsifier other than an acrylic resin having an ammonium group

Hexadecyltrimethylammonium chloride (7 parts) was put in a reaction container as an emulsifier and dissolved in 300 parts of ion-exchanged water, and the dissolved solution was heated

under stirring at 75°C. An aqueous solution of 1 part of 2,2'-azobis(2-(2-imidazoline-2-yl)propane) neutralized wholly with acetic acid was added dropwise thereto over 5 minutes. The mixed solution was aged for 5 minutes and, then, 10 parts of methyl methacrylate was added dropwise thereto over 5 minutes. The mixture was further aged for 5 minutes, and preemulsion, which was obtained by adding an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture consisting of 140 parts of methyl methacrylate, 30 parts of styrene, 25 parts of n-butyl methacrylate, 5 parts of glycidyl methacrylate and 25 parts of neopentyl glycol dimethacrylate to a mixed solution of 22 parts of hexadecyltrimethylammonium chloride and 270 parts of ion-exchanged water under stirring, was added dropwise thereto over 40 minutes. This mixture was aged for 60 minutes and, then, cooled to obtain an aqueous dispersion of a crosslinked resin particle 5, which had a non-volatile content of 30%, a pH of 5.2 and a volume-average particle diameter of 120 nm. This aqueous dispersion was mixed with xylene to form a mixture and xylene was substituted for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a crosslinked resin particle 5 in xylene.

#### Production Example 12

##### Production of a non-crosslinked resin particle

In a reaction container, 20 parts of the acrylic resin 1 having an ammonium group, produced in Production Examples 4, and 300 parts of ion-exchanged water were put, and the mixture was heated under stirring at 75°C. An aqueous solution of 1 part of 2,2'-azobis(2-(2-imidazoline-2-yl)propane) neutralized wholly with acetic acid was added dropwise thereto over 5 minutes. The mixed solution was aged for 5 minutes and, then, 10 parts of methyl methacrylate was added dropwise thereto over 5 minutes. The mixture was further aged for 5 minutes, and preemulsion, which was obtained by adding an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture containing no



poly(meth)acrylate, consisting of 140 parts of methyl methacrylate, 30 parts of styrene, 25 parts of n-butyl methacrylate and 5 parts of glycidyl methacrylate, to an aqueous solution of 55 parts of the acrylic resin 1 having an ammonium group and 270 parts of ion-exchanged water under stirring, was added dropwise thereto over 40 minutes. This mixture was aged for 60 minutes and, then, cooled to obtain an aqueous dispersion of a non-crosslinked resin particle. The resulting aqueous dispersion of the non-crosslinked resin particle had a non-volatile content of 32.8%, a pH of 5.0 and a volume-average particle diameter of 106 nm. This aqueous dispersion was mixed with xylene to form a mixture and xylene was substituted for water being a solvent of the mixture while the mixture was azeotropically distilled in an evaporator to obtain a dispersion of a non-crosslinked resin particle in xylene.

#### Production Example 13

Production of an epoxy resin composition having a sulfonium group and a propargyl group

In a separable flask provided with a stirrer, a thermometer, a nitrogen gas inlet tube and a reflux cooling tube, 100.0 parts of EPOTOHTO YDCN-701 with an epoxy equivalent of 200.4 (cresol novolak type epoxy resin made by Tohto Kasei Co., Ltd.), 23.6 parts of propargyl alcohol and 0.3 part of dimethylbenzylamine were put, and the mixture was heated to 105°C and reacted at that temperature for 3 hours to obtain a resin composition containing a propargyl group with an epoxy equivalent of 1580. Acetylacetonate-copper (2.5 parts) was added thereto, and the reaction was allowed to proceed at 50°C for 1.5 hours. It was verified that part of the terminal hydrogens of the added propargyl groups was disappeared by proton (1H) NMR (propargyl converted to acetylide equivalent to 14 milli moles per 100 g of the resin solid matter).

1-(2-hydroxyethylthio)-2,3-propanediol (10.6 parts), 4.7 parts of glacial acetic acid and 7.0 parts of deionized water were

added thereto, and the reaction was allowed to proceed for 6 hours while maintaining the temperature at 75°C. After verification that the residual acid value is 5 or less, 43.8 parts of deionized water was added to give an intended resin composition solution. This solution had a solid matter content of 70.0 % by weight and the sulfonium value of 28.0 milli moles per 100 g varnish. The number-average molecular weight, measured by GPC, was 2443.

10 Production Example 14

Production of a cationic electrocoating

To 142.9 parts of the resin composition obtained in Production Example 13 was added 157.1 parts of deionized water, and the mixture was stirred in a high-speed rotary mixer for 1 hour and, then, this aqueous solution was adjusted so as to have a solid matter content of 15 % by weight to obtain a cationic electrocoating.

Production Example 15

20 Production of a cationic electrocoating

The resin composition obtained in Production Example 13 (142.9 parts) and 157.1 parts of deionized water were mixed and, to this mixture, the aqueous dispersion of the crosslinked resin particle 1 obtained in Production Example 9 was further added in such a manner that the solid matter content of the dispersion is 20 % by weight relative to the resin solid matter in the coating. After the mixture was stirred in a high-speed rotary mixer for 1 hour, 373.3 parts of deionized water was added and this aqueous solution was adjusted so as to have a solid matter content of 15 % by weight to obtain a cationic electrocoating.

Production Examples 16 to 19

Production of a cationic electrocoating

Cationic electrocoatings were obtained by following the same procedure as in Production Example 15 except for using the

aqueous dispersion of crosslinked resin particles 2 to 5 obtained in Production Examples 8 to 11 in place of the aqueous dispersion of the crosslinked resin particle 1 obtained in Production Example 7.

5

#### Production Example 20

##### Production of a cationic electrocoating

Cationic electrocoating was obtained by following the same procedure as in Production Example 15 except for using the aqueous dispersion of non-crosslinked resin particle obtained in Production Example 12 in place of the aqueous dispersion of the crosslinked resin particle 1 obtained in Production Example 7.

10

#### Production Example 21

##### 15 Production of a crosslinked resin particle 6

Into a separable flask provided with a dropping funnel, a thermometer, a nitrogen gas inlet tube, a reflux cooling tube and a stirrer were charged 289.6 parts of ion-exchanged water and 10.3 parts of a resin dilution solution prepared by diluting the epoxy resin composition produced in Production Example 13 until the solid matter content of the epoxy resin composition reaches 36.1%. The temperature of this mixture was raised to 70°C under being stirred in a nitrogen atmosphere. An aqueous solution consisting of 20.0 parts of ion-exchanged water, 0.5 part of VA-061 (azo initiator produced by Wako Pure Chemical Industries, Ltd.) and 0.3 part of an 90% aqueous solution of acetic acid was added thereto dropwise over 5 minutes. To this mixture, a preemulsion, which was prepared by adding a monomer mixture consisting of 80 parts of styrene and 20 parts of divinylbenzene to an emulsifier solution formed by dissolving 20.5 parts of a resin dilution solution identical to the above one in 130 parts of ion-exchanged water and by emulsifying the resulting mixture with a mixer, was added dropwise from a dropping funnel constantly over 75 minutes. After the completion of the dropwise addition, the preemulsion mixture was aged at that

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temperature for 60 minutes and then cooled. With the addition of ion-exchanged water, a dispersion of a crosslinked resin particle 6, having a nonvolatile content of 20%, was obtained. The resulting dispersion of the crosslinked resin particle 6  
5 had a pH of 4.8 and a volume-average particle diameter of 100 nm.

#### Production Example 22

##### Production of a cationic electrocoating

10 A cationic electrocoating was obtained by following the same procedure as in Production Example 15 except for using the dispersion of the crosslinked resin particle 6 obtained in Production Example 21 in place of the dispersion of the crosslinked resin particle 1 obtained in Production Example 7  
15 and preparing a coating in such a manner that a solid matter content was equivalent to that in Production Example 15.

#### Production Example 23

##### Production of a crosslinked resin particle 7

20 Into a separable flask provided with a dropping funnel, a thermometer, a nitrogen gas inlet tube, a reflux cooling tube and a stirrer were charged 289.0 parts of ion-exchanged water and 10.0 parts of AQUARON HS-10  
( $\alpha$ -sulfo- $\omega$ -[2-(1-propenyl)-4-nonyl-phenoxy]polyoxyethylene  
25 (n=10) ammonium salt, made by Daiichi Kogyo Seiyaku Co., Ltd.), and the temperature of this mixture was raised to 80°C in a nitrogen atmosphere. Aside from this mixture, a preemulsion was prepared by adding a monomer mixture solution consisting of 13 parts of styrene, 42 parts of methyl methacrylate and 45 parts of ethylene  
30 glycol dimethacrylate to an emulsifier solution formed by dissolving 5.0 parts of AQUARON HS-10 in 134.5 parts of ion-exchanged water and by emulsifying the resulting mixture with a mixer. To the mixture described above, the preemulsion thus prepared and an initiator solution formed by dissolving  
35 0.5 part of ammonium persulfate in 36.7 parts of ion-exchanged

water were added dropwise simultaneously from two separate dropping funnels. The preemulsion was added constantly over 60 minutes and the initiator solution constantly over 75 minutes. After the completion of the dropwise addition, the resulting  
5 mixture was aged at that temperature for 60 minutes and then cooled. With the addition of ion-exchanged water, a dispersion of a crosslinked resin particle 7, having a nonvolatile content of 15 %, was obtained. The resulting dispersion of the  
10 crosslinked resin particle 7 had a pH of 7.3 and a volume-average particle diameter of 80 nm.

#### Production Example 24

##### Production of a cationic electrocoating

A cationic electrocoating was obtained by following the  
15 same procedure as in Production Example 15 except for using the dispersion of a crosslinked resin particle 7 obtained in Production Example 23 in place of the dispersion of a crosslinked resin particle 1 obtained in Production Example 7 and preparing a coating in such a manner that a solid content was equivalent  
20 to that in Production Example 15.

#### Examples 1 to 6

By using the cationic electrocoatings obtained in Production Examples 15 to 19, and 22 respectively, insulating  
25 films were formed on the surface of copper square wires (a cross section profile being square and having a size of 0.3 mm × 0.3 mm, and the curvature being 10%) by subjecting the square wires respectively to the following pretreatment means, electrodeposition means, washing means and heating means.

##### 30 [Pretreatment means]

(1) The electric wire was degreased with SURF POWER (made by NIPPON PAINT Co., Ltd.) at a treatment temperature of 45°C for a treatment time of 60 seconds.

(2) The degreased electric wire was washed with water by spraying  
35 for 30 seconds.

[Electrodeposition means]

The wire after water washing was immersed in the cationic electrocoatings obtained in Production Examples 15 to 19, and 22 stored as an electrocoating bath liquid in an electrocoating bath and cationic electrodeposited at a bath temperature of 30°C for 5 seconds with a voltage of 100 V being applied (with the wire as the cathode and the counter electrode as the anode). Here, in each of the examples, the electrocoating bath having a shape shown in Fig. 3 was used under conditions of a shifting speed of the square wire of 15 m/min and a ratio of (shortest distance of the square wire from liquid-contact portion with cationic electrocoating to electrode) / (total shift distance of square wire from liquid-contact portion to liquid-separation portion in the electrocoating bath) = 3/4.

15 [Washing means]

Each of the wires obtained after immersion period of cationic electrodeposition was washed with water by spraying for 30 seconds to remove the cationic electrocoating adhering to the wire.

20 [Heating means]

Each of the wires after washing was heated in a hot air drying oven at 190°C for 25 minutes to form an insulating film and give an insulated wire.

25 Comparative Example 1

An insulated wire of a square wire was obtained by following the same procedure as in Example 1 except that in place of the cationic electrocoating obtained in Production Example 15, a cationic electrocoating obtained in Production Example 14 was used.

30

Comparative Example 2

An insulated wire of a square wire was obtained by following the same procedure as in Example 1 except that in place of the cationic electrocoating obtained in Production Example 15, a

35

cationic electrocoating coating obtained in Production Example 20 was used.

#### Example 7

- 5           An insulated wire was obtained by following the same procedure as in Example 1 except that in place of the cationic electrocoating obtained in Production Example 15, a cationic electrocoating obtained in Production Example 24 was used.

#### 10   Example 8

          An insulated wire was obtained by following the same procedure as in Example 1 except that the cationic electrocoating obtained in Production Example 15 was used and that an electrocoating bath shown in Fig. 4 was used.

15

#### Example 9

- An insulated wire was obtained by following the same procedure as in Example 1 except that the cationic electrocoating obtained in Production Example 15 was used and that an  
20   electrocoating bath shown in Fig. 3 was used under conditions of a shifting speed of 30 m/min and a ratio of shortest shift distance/shift distance = 3/4.

#### Comparative Example 3

- 25           An insulated wire was obtained by following the same procedure as in Example 1 except that the cationic electrocoating obtained in Production Example 15 was used and that a shifting speed of a square wire was set to 100 m/min.

#### 30   Comparative Example 4

- An insulated wire was obtained by following the same procedure as in Example 1 except that the cationic electrocoating obtained in Production Example 15 was used and that a coating process was carried out at a ratio of (shortest distance of the  
35   square wire from liquid-contact portion with cationic

electrodeposition coating to electrode) / (total shift distance of square wire from liquid-contact portion to liquid-separation portion in the electrocoating bath) = 1/1.5.

5    Reference Example 1

        An insulated wire of a round wire was obtained by following the same procedure as in Example 1 except that in place of a square wire, a round wire having a round shape in the cross-sectional profile and having a diameter of 0.4 mm was used.

10

        [Evaluation]

        The insulated wires of a square wire obtained in Examples 1 to 9 and Comparative Examples 1 to 4 were evaluated on a dielectric breakdown voltage using a withstand voltage  
15    insulation tester (Model 8525 manufactured by Tsuruga Electric Co.) by the metal foil method according to JISC 3003. The results are shown in Table 1.

        Moreover, each of the insulated wires obtained by Example 1 and Reference Example 1 was wound around a coil former having  
20    a diameter of 100 mm manually 1000 times to prepare a coil, and the measured electric resistances of the coils were respectively 11Ω and 16Ω.



Table 1

	Dielectric breakdown voltage (kV)
Ex. 1	2.5
Ex. 2	2.8
Ex. 3	2.4
Ex. 4	2.3
Ex. 5	2.8
Ex. 6	3.0
Ex. 7	2.0
Ex. 8	2.5
Ex. 9	2.5
Compar. Ex. 1	0.4
Compar. Ex. 2	0.6
Compar. Ex. 3	0.8
Compar. Ex. 4	0.9

As is clear from Table 1, the insulated wire of a square wire obtained in each of Examples had dielectric breakdown voltage higher than those obtained in Comparative Examples. Moreover, the roll wire obtained from the insulated wire of a square wire of the present invention had smaller electric resistance in comparison with a roll wire obtained from a round wire.

10

#### Production Example 25

##### Production of an insulating coating

The dispersion of a crosslinked resin particle 1 in xylene obtained in Production Example 7 was added to NEOHEAT AI (polyamide-imide resin coating, made by Totoku Toryo Co., Ltd., resin solid matter in a coating composition: 40% by weight) in such a way that the amount of this dispersion is 20% by weight relative to the resin solid matter in the coating composition,

15

and the mixture was stirred for 1 hour with a mixer. Thereafter, xylene was added to the mixture in such a way that the concentration of the solid matter is 15% by weight to obtain an insulating coating.

5

Production Examples 26 to 29

Production of insulating coatings

Respective insulating coatings were obtained by following the same procedure as in Production Example 25 except for using the dispersions of crosslinked resin particles 2 to 5 in xylene obtained in Production Examples 8 to 11, respectively, in place of the dispersion of a crosslinked resin particle 1 in xylene obtained in Production Example 7.

15 

Production Example 30

Production of an insulating coating

A coating composition was obtained by following the same procedure as in Production Example 25 except for using the dispersion of a non-crosslinked resin particle in xylene obtained in Production Example 12 in place of the dispersion of a crosslinked resin particle 1 in xylene obtained in Production Example 7.

Examples 10 to 25

25 A first insulating film was formed on the surface of a square wire by following the same procedure as in Example 1 except that each of the cationic electrocoatings shown in Table 2 was used.

30 The resulting electric wire on which the first insulating film was formed was immersion-coated with the insulating coatings shown in Table 2, and then heated at 190°C for 8 minutes. By repeating this cycle of applying the insulating coating and heat setting 3 times, the second insulating film was formed to obtain insulated wires of a square wire.

35

## Comparative Example 5

An insulated wire of a square wire was obtained by following the same procedure as in Example 10 except that in place of the cationic electrocoating obtained in Production Example 15, the  
5 cationic electrocoating obtained in Production Example 14 was used, and that in place of the insulating coating obtained in Production Example 25, NEOHEAT AI was used.

## Comparative Example 6

10 An insulated wire of a square wire was obtained by following the same procedure as in Example 10 except that in place of the cationic electrocoating obtained in Production Example 15, the cationic electrocoating obtained in Production Example 14 was used, and that in place of the insulating coating obtained in  
15 Production Example 25, an insulating coating obtained in Production Example 30 was used.

## Reference Example 2

20 An insulated wire of a round wire was obtained by following the same procedure as in Example 10 except that in place of a square wire, a round wire having a round shape in the cross-sectional profile and having a diameter of 0.4 mm was used.

## [Evaluation]

25 The insulated wires of a square wire obtained in Examples 10 to 25 and Comparative Examples 5 and 6 were evaluated on a dielectric breakdown voltage using a withstand voltage insulation tester (Model 8525 manufactured by Tsuruga Electric Co.) by the metal foil method according to JISC 3003. The results  
30 are shown in Table 2.

Moreover, each of the insulated wires obtained by Example 10 and Reference Example 2 was wound around a coil former having a diameter of 100 mm manually 1000 times to prepare a coil, and the measured electric resistances of the coils were respectively  
35 11 $\Omega$  and 16 $\Omega$ .

Table 2

		Example										Compar. Ex.	
		10	11	12	13	14	15	16	17	18			
Cationic electrocoating	Production Example	15	16	17	18	19	15	16	17	18			
	Crosslinked resin particle contained	7	8	9	10	11	7	8	9	10			
Insulating coating	Production Example	25	26	27	28	29	NEO <sup>1)</sup>	NEO <sup>1)</sup>	NEO <sup>1)</sup>	NEO <sup>1)</sup>			
	Crosslinked resin particle contained	7	8	9	10	11	-	-	-	-			
Dielectric breakdown voltage (kV)		8.2	7.5	8.0	7.6	8.1	5.0	4.7	5.4	4.9			
		Example										Compar. Ex.	
		19	20	21	22	23	24	25	26	27	28		
Cationic electrocoating	Production Example	19	14	14	14	14	14	22	24	14	14	14	
	Crosslinked resin particle contained	11	-	-	-	-	-	21	23	-	-	-	
Insulating coating	Production Example	NEO <sup>1)</sup>	25	26	27	28	29	27	27	NEO <sup>1)</sup>	30		
	Crosslinked resin particle contained	-	7	8	9	10	11	9	9	-	12 <sup>2)</sup>		
Dielectric breakdown voltage (kV)		5.0	3.4	3.5	3.7	3.5	3.5	8.2	7.1	0.5	0.9		

1)NEO means NEOHEAT AI (polyamide-imide resin coating manufactured by TOTOKU TORYO Co., Ltd.)

2)In Production Example 12, a non-crosslinked resin particle is used.

As is clear from Table 2, the insulated wire of a square wire obtained in each of Examples had dielectric breakdown voltage higher than those obtained in Comparative Examples. In particular, when the cationic electrocoating and insulating coating containing crosslinked resin particles obtained by emulsion polymerizing using a resin having an ammonium group or a sulfonium group as an emulsifier (Examples 10 to 13 and 25), the dielectric breakdown voltage thereof becomes higher. Moreover, the roll wire, obtained from the insulated wire of a square wire of the present invention, had smaller electric resistance in comparison with a roll wire obtained from a round wire.

#### INDUSTRIAL APPLICABILITY

The method of coating a square wire of the present invention, which has the above-mentioned constitution, makes it possible to obtain an insulated wire of a square wire having a high dielectric breakdown voltage. Moreover, since the insulated wire of a square wire is allowed to have a higher occupancy ratio, it has improved performances in comparison with the application of a round wire having the same volume, and is desirably used as a magnet wire and the like. Therefore, the insulated wire of a square wire, obtained by the method of coating a square wire of the present invention, can be desirably used in various applications as an insulated wire with a high dielectric breakdown voltage. Further, the roll wire, obtained from the insulated wire of a square wire of the present invention, has smaller electric resistance, and is desirably applicable to various coils.

## CLAIMS

1. A method of coating a square wire comprising a step of:

5 carrying out cationic electrodeposition on a square wire to form an insulating film thereon, by using a cationic electrocoating that stored in an electrocoating bath,

wherein the shifting speed of the square wire in the electrocoating bath is set in a range from 1 to 80 m/min;

10 the shortest distance from a liquid-contact portion of the square wire onto the cationic electrocoating to an electrode is set longer than 1/2 of the total shift distance of the square wire from the liquid-contact portion of the square wire to a liquid-separation portion in the electrocoating bath,

15 the cationic electrocoating contains a resin composition of which a hydratable functional group is reduced directly by electrons and passivated, resulting in deposition of a film, and

20 the cationic electrocoating contains crosslinked resin particles.

2. The method of coating a square wire according to Claim 1,

25 wherein the crosslinked resin particle being one of which a hydratable functional group is reduced directly by electrons and passivated.

3. The method of coating a square wire according to Claim 1 or 2,

30 wherein the content of the crosslinked resin particles is 0.5 to 40 % by weight.

4. The method of coating a square wire according to any of Claims 1 to 3,

35 wherein the crosslinked resin particle is obtained by

emulsion polymerizing an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture using a resin having an onium group as an emulsifier.

5     4,     5. The method of coating a square wire according to Claim  
         wherein the resin having an onium group has 2 to 15 onium  
         groups per one molecule.

10    4 or 5,     6. The method of coating a square wire according to Claim  
         wherein the resin having an onium group is an acrylic resin  
         or an epoxy resin.

15    of Claims 4 to 6,     7. The method of coating a square wire according to any  
         wherein the onium group is an ammonium group or a sulfonium  
         group.

20    7,     8. The method of coating a square wire according to Claim  
         wherein the acrylic resin or the epoxy resin, having the  
         ammonium group or the sulfonium group, is obtained by adding  
         a tertiary amine compound or sulfide and an organic acid to an  
         acrylic resin or an epoxy resin, having an epoxy group, to convert  
25    the acrylic resin or the epoxy resin to a quaternary ammonium  
         compound or a tertiary sulfonium compound.

30    8,     9. The method of coating a square wire according to Claim  
         wherein a number-average molecular weight of the acrylic  
         resin or the epoxy resin, having an epoxy group, is 2000 to 20000.

35    wherein the resin composition has a sulfonium group and  
         10. The method of coating a square wire according to any  
         of Claims 1 to 9,

a propargyl group.

11. The method of coating a square wire according to any of Claims 1 to 10,

5        wherein the resin composition has a sulfonium group content of 5 to 400 milli moles, a propargyl group content of 10 to 495 milli moles and a total content of the sulfonium and propargyl groups of 500 milli moles or less, per 100 g of the solid matter in the resin composition.

10

12. The method of coating a square wire according to any of Claims 1 to 11,

      wherein the resin composition includes an epoxy resin having a novolak cresol epoxy resin or a novolak phenol epoxy resin as a skeleton and having a number-average molecular weight  
15        of 700 to 5000, and

      the resin composition also has a sulfonium group content of 5 to 250 milli moles; a propargyl group content of 20 to 395 milli moles and a total content of the sulfonium and propargyl  
20        groups of 400 milli moles or less, per 100 g of the solid matter in the resin composition.

13. An insulated wire of a square wire which is obtained by the method of coating a square wire according to any of Claims  
25        1 to 12.

14. A roll wire which is obtained from the insulated wire of a square wire according to Claim 13.

30        15. A method of coating a square wire, comprising a step (I) of forming a first insulating film by cationic electrodeposition using a cationic electrocoating, and a step (II) of forming a second insulating film on the first insulating film formed in the step (I) using an insulating coating,

35        wherein the shifting speed of the square wire in the



electrocoating bath is set in a range from 1 to 80 m/min;

the shortest distance from a liquid-contact portion of the square wire onto the cationic electrocoating to an electrode is set longer than 1/2 of the total shift distance of the square wire from the liquid-contact portion of the square wire to a liquid-separation portion in the electrocoating bath, and

wherein said cationic electrocoating contains a resin composition of which a hydratable functional group is reduced directly by an electron and passivated, resulting in deposition of a film and

said cationic electrocoating and/or the insulating coating contains crosslinked resin particles.

16. The method of coating a square wire according to Claim 15,

wherein the cationic electrocoating contains crosslinked resin particles.

17. The method of coating a square wire according to Claim 15 or 16,

the crosslinked resin particle being one of which a hydratable functional group is reduced directly by electrons and passivated.

18. The method of coating a square wire according to any of Claims 15 to 17,

wherein the content of the crosslinked resin particles is 0.5 to 40 % by weight in the coating.

19. The method of coating a square wire according to any of claims 15 to 18,

wherein the crosslinked resin particle is obtained by emulsion polymerizing an  $\alpha,\beta$ -ethylenically unsaturated monomer mixture using a resin having an onium group as an emulsifier.

20. The method of coating a square wire according to Claim 19,

wherein the resin having an onium group has 2 to 15 onium groups per one molecule.

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21. The method of coating a square wire according to Claim 19 or 20,

wherein the emulsifier is an acrylic resin or an epoxy resin.

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22. The method of coating a square wire according to any of Claims 19 to 21,

wherein the onium group is an ammonium group or a sulfonium group.

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23. The method of coating a square wire according to Claim 22,

wherein the acrylic resin or the epoxy resin, having the ammonium group or the sulfonium group, is obtained by adding a tertiary amine compound or sulfide and an organic acid to an acrylic resin or an epoxy resin, having an epoxy group, to convert the acrylic resin or the epoxy resin to a quaternary ammonium compound or a tertiary sulfonium compound.

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24. The method of coating a square wire according to Claim 23,

wherein a number-average molecular weight of the acrylic resin or the epoxy resin, having an epoxy group, is 2000 to 20000.

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25. The method of coating a square wire according to any of Claims 15 to 24,

wherein the resin composition has a sulfonium group and a propargyl group.

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26. The method of coating a square wire according to any

of Claims 15 to 25,

wherein the resin composition has a sulfonium group content of 5 to 400 milli moles, a propargyl group content of 10 to 495 milli moles and a total content of the sulfonium and propargyl groups of 500 milli moles or less, per 100 g of the solid matter in the resin composition.

27. The method of coating a square wire according to any of Claims 15 to 26,

wherein the resin composition includes an epoxy resin having a novolak cresol epoxy resin or a novolak phenol epoxy resin as a skeleton and having a number-average molecular weight of 700 to 5000, and

the resin composition also has a sulfonium group content of 5 to 250 milli moles, a propargyl group content of 20 to 395 milli moles and a total content of the sulfonium and propargyl groups of 400 milli moles or less, per 100 g of the solid matter in the resin composition.

28. An insulated wire of a square wire which is obtained by the method of coating a square wire according to any of Claims 15 to 27.

29. A roll wire which is obtained from the insulated wire of a square wire according to Claim 28.

Fig. 1

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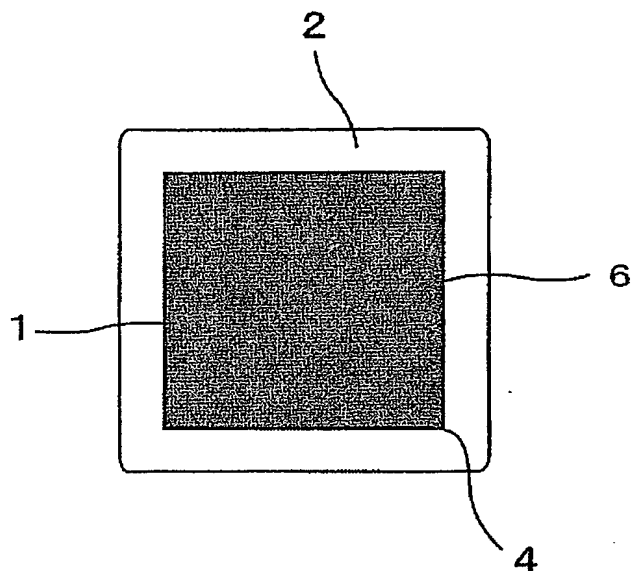


Fig. 2

5

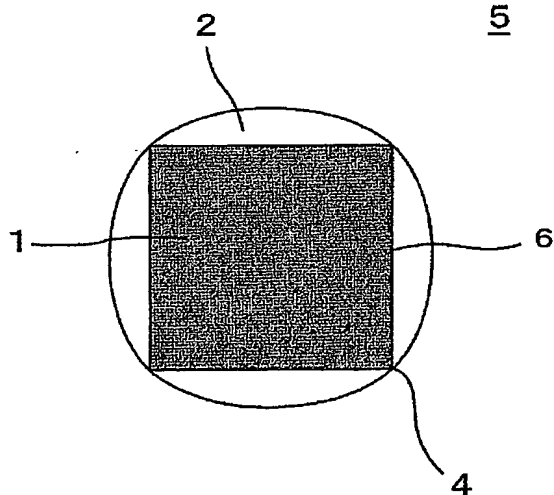


Fig. 3

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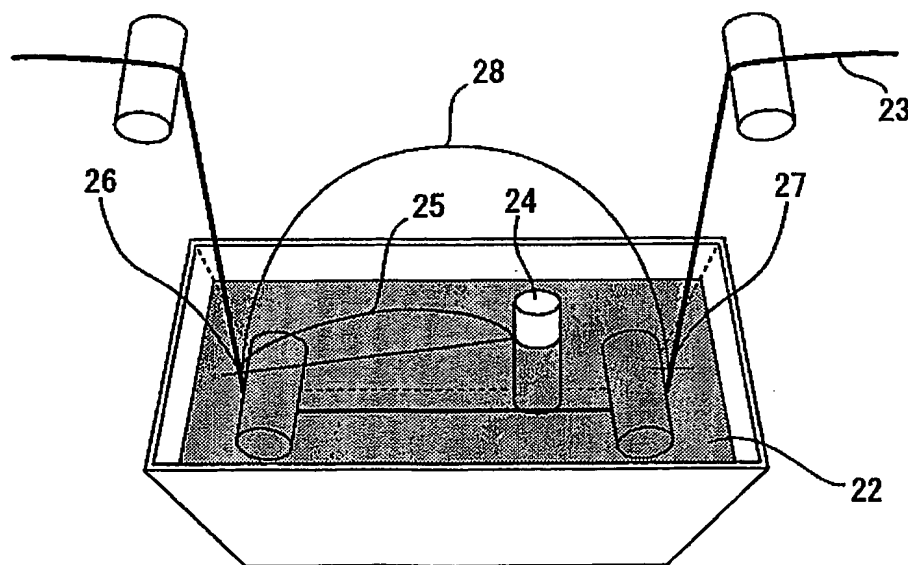
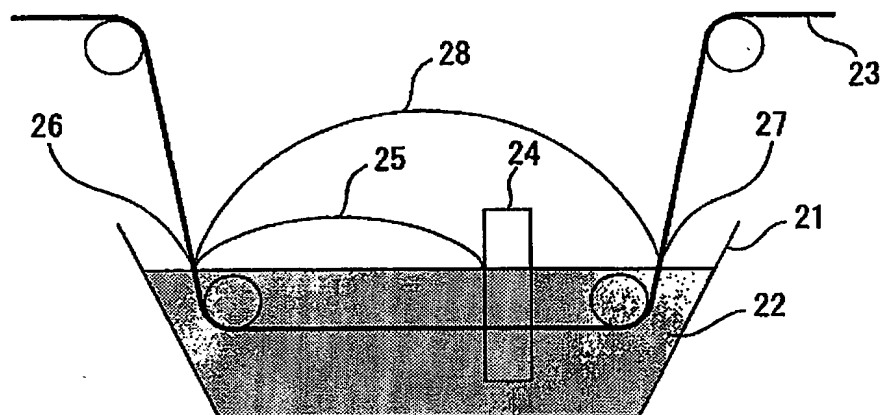
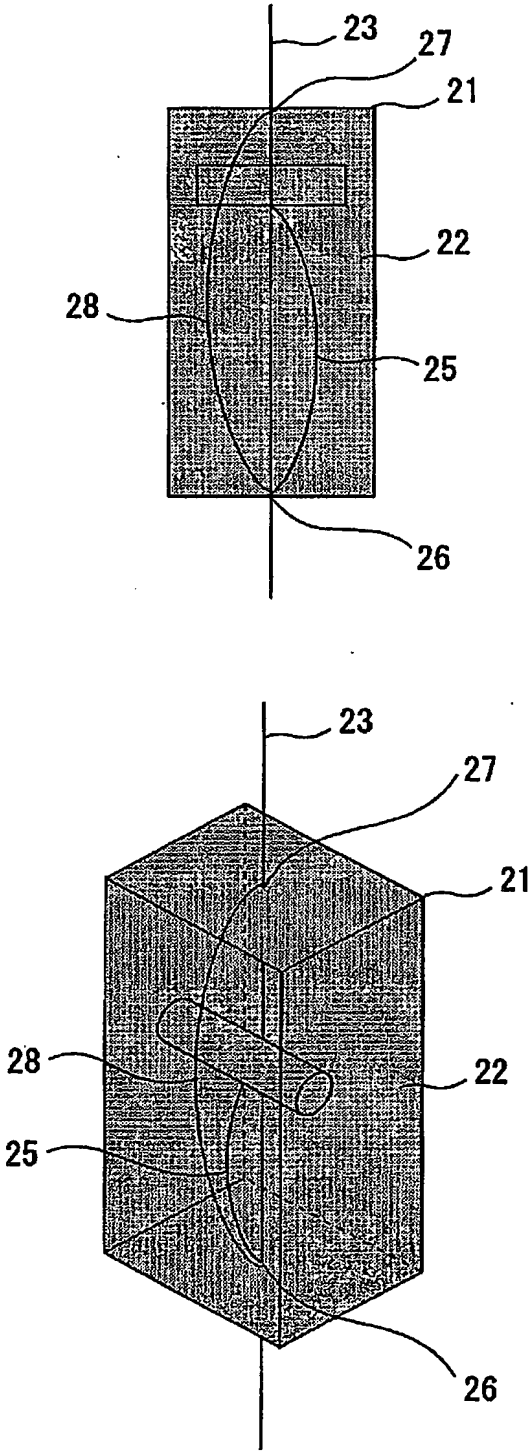


Fig. 4

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Fig. 5

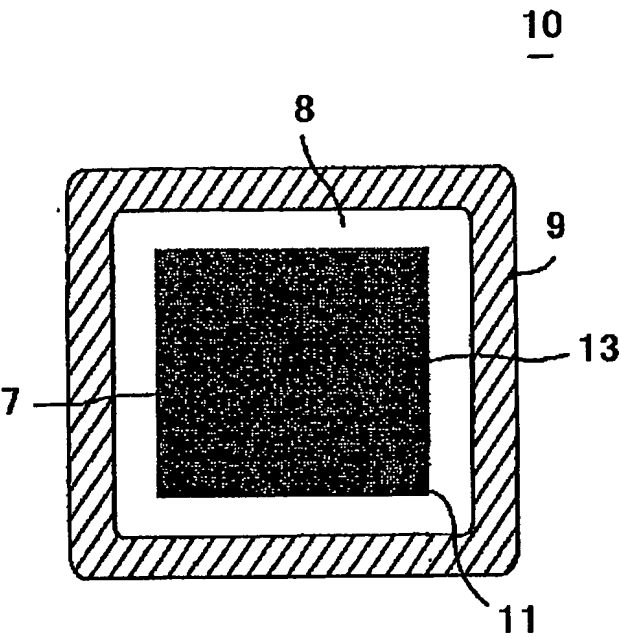


Fig. 6

